*Formation and Aging of Precipitates. I. Electron Microscopic Studies of the Formation of Barium Sulfate Precipitate**

By Eiji SUITO and Kazuyoshi TAKIYAMA

(Received September 17, 1953)

Introduction

The relations between the formation of the precipitates and their physical and chemical properties have been studied by a number of investigators. Especially the precipitation of barium sulfate has been investigated as a fundamental case. Fischer[1] and Okada[2] employed the electron microscope to study the precipitates of barium sulfate. The authors also used an electron microscope to study the formation, the aging and the growth mechanism of the crystals of barium sulfate. In this paper the relation between the concentration of the reagents and the shape and size of the precipitated particles is described.

Experimental Procedure

Barium sulfate precipitates were formed on mixing barium hydroxide with sulfuric acid to keep out the disturbance of other ions. But at concentrations higher than 0.2 M barium acetate and manganous sulfate were used because of their solubilities. These reagents were all guaranteed. The reagents of equal volumes and of the same concentrations were mixed rapidly by pouring into a large test tube at 18°C. Directly after mixing, a drop of the reaction products was placed on a specimen holder for the electron microscope and was dried. The specimens were observed directly or after chromium shadowing by the electron microscope SM—T4.

Experimental Results

Fifteen kinds of precipitates were prepared, varying the total concentration of barium sulfate from 1.0000 to 0.0001 M (i.e. the concentration of the reagents from 2.0000 to 0.0002 M). Several specimens for electron microscopy were prepared from each precipitate, and several electron micrographs were taken for each of the specimens. The shape and the size of the particles of each precipitate were observed, then the length of the longest part of the particles was measured. From about 200 particles the size distribution curves of each precipitate were obtained as shown in Fig. 1, in which the relative frequency is plotted against the length of the particle. These distribution curves are for

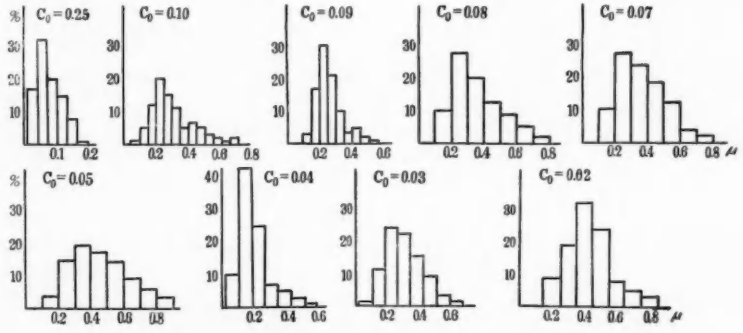

Fig. 1. Frequency histogram of particle size.
abscissa: size of particles (μ).
ordinate: relative frequency (% of particles).

the samples ranging from 0.25 to 0.02 M in the total concentration. From these distribution curves the arithmetic mean sizes of the particles were calculated. The shape and the size of barium sulfate precipitates formed in different total concentrations are shown collectively in Table 1.

* Some parts of this experiment were published in *Proc. Japan Acad.*, **28**, 133 (1952) as a preliminary report.

1) R. B. Fischer, *Anal. Chem.*, **23**, 1667 (1951).

2) S. Okada, M. Kawane and S. Magari, *Mem. Faculty Eng. Kyoto Univ.*, **13**, 198 (1951).

TABLE I

THE RELATION OF THE SHAPE AND SIZE TO THE TOTAL CONCENTRATION OF BARIUM SULFATE PRECIPITATES

Group	No.	Total concentration C_0(M)	Particle size (mean) L(mμ)	$C_0 \times L$	Particle shape
A	1	1.00	13	13.0	Amorphous
„	2	0.50	25	12.5	„
„	3	0.25	51	12.7	Sphere
B	4	0.10	251	25.1	Spindle
„	5	0.09	266	23.9	„
„	6	0.08	307	24.5	„
„	7	0.07	317	22.2	„
„	8	0.05	470	23.5	„
C	9	0.04	182	7.3	Cross spindle
„	10	0.03	270	8.1	„
„	11	0.02	466	9.3	„
D	12	0.01	1650	16.5	Diamond (rugged)
E	13	0.001	2030	20.3	Diamond (round)
F	14	0.0003	850	0.255	Rectangle
„	15	0.0001	110	0.011	„

I. The Shape of Barium Sulfate Precipitates.

The natural habit of barium sulfate is orthorhombic. But several kinds of different shapes were formed by changing the total concentrations as shown in Table I. The degree of perfection of the crystals was excellent at lower concentration.

At the total concentration of 1.0 M the colorless and transparent jelly was formed immediately after mixing the reagents. This jelly turned white in a few minutes. The precipitates prepared over the range 1.0 to 0.5 M in the total concentrations were jelly or gel. One of the electron micrographs is shown in Photo 1. It seems to be in an amorphous state according to the resolving power of the electron microscope used today. At the total concentration of 0.25 M the precipitate was crystalline, each particle being an irregular sphere as shown in Photo 3.

It seemed that the precipitates prepared in this range (A group in Table I) were affected by acetate and manganous ions. When barium hydroxide saturated in boiling water reacted with 6 N sulfuric acid, beautiful spherical particles, 80 mμ in diameter, were formed.

In the range of the total concentrations, 0.10~0.05 M (B group), the powdery precipitates appeared directly after mixing the reagents and the shape of the precipitated particles was like a spindle with rugged edges as shown in Photo 4. The ratio of major axis to minor axis was almost constant, namely, 10 : 5.5. The number of projections was eight or ten, and the crystal seemed to have grown in the direction of the projections.

In the range of the total concentrations, 0.04~0.02 M (C group), many cross spindle shaped particles were found besides simple spindle shaped ones as shown in Photo 5. The both lengths of the cross spindles were the same and the projections decreased in number.

At the total concentration of 0.01 M (D group) the precipitate appeared a few seconds after mixing the reagents, and it was diamond shaped having rugged edges as shown in Photo 7. The particles were flat and the ratio of thickness to length was 1 : 10.

At the total concentration of 0.001 M (E group) the precipitate formed about ten seconds after mixing the reagents and consisted of large diamond shaped particles having smooth edges and small spindle shaped ones, which were about 1/10 in size of the large ones, as shown in Photo 8.

In the range of the total concentrations below 0.0003 M (F group) the precipitates appeared about one or two minutes after mixing the reagents. The particles sampled before the completion of the crystals were flat and rectangular, consisting of irregular sizes as shown in Photo 10.

II. The Particle Size of Barium Sulfate Precipitates.

The size of particles of freshly precipitated barium sulfate generally increased with the decrease of the total concentration as shown in Table I. In the A, B and C groups, each of which has the same shape, the relation of the total concentration C_0 (M) to the size

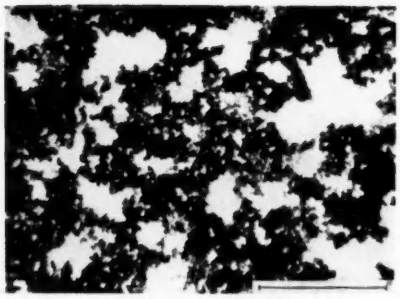

Photo. 1. C_0=1.0 M
(×20,000)

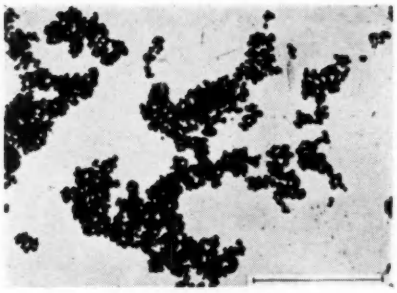

Photo. 2. C_0=1.0 M
After 3 months (×20,000)

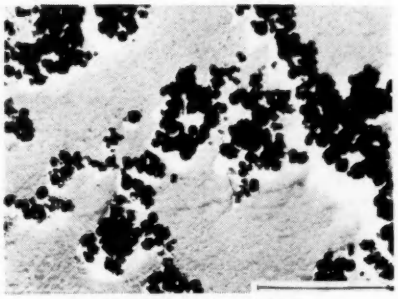

Photo. 3. C_0=0.25 M
(Cr-shadowing, ×20,000)

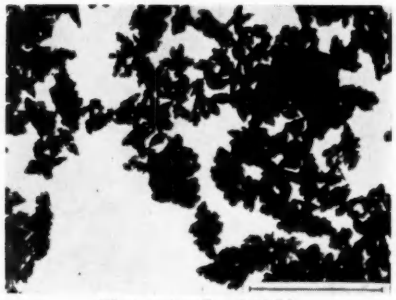

Photo. 4. C_0=0.10 M
(×20,000)

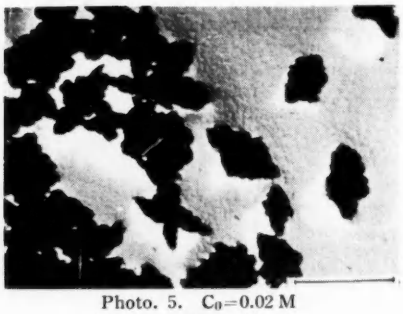

Photo. 5. C_0=0.02 M
(Cr-shadowing, ×15,000)

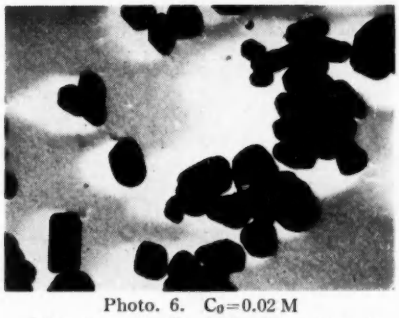

Photo. 6. C_0=0.02 M
After 2 years (Cr-shadowing, ×15,000)

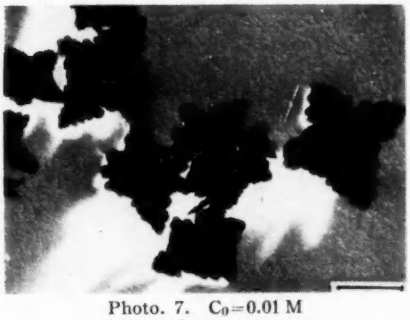

Photo. 7. C_0=0.01 M
(Cr-shadowing, ×10,000)

Photo. 8. C_0=0.001 M
(×10,000)

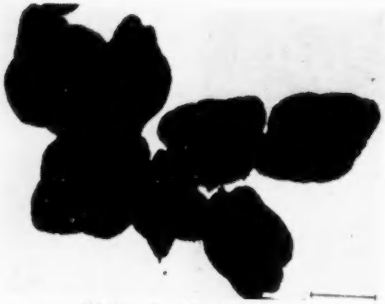

Photo. 9. C_0=0.001 M
After 5 hours (×10,000)

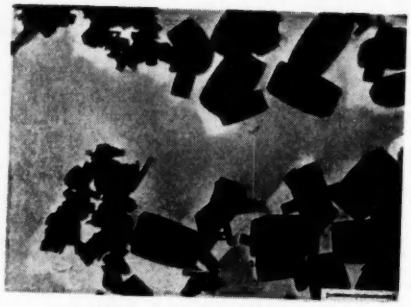

Photo. 10. C_0=0.0003 M
(Cr-shadowing, ×10,000)

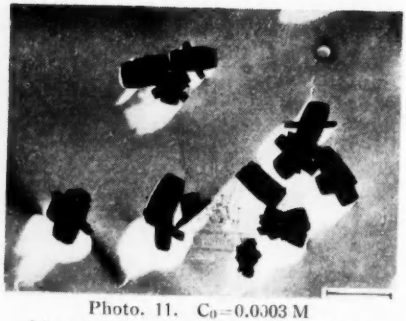

Photo. 11. C_0=0.0003 M
After 5 hours (Cr-shadowing, ×10,000)

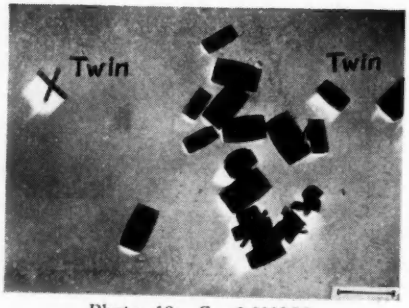

Photo. 12. C_0=0.0003 M
(Cr-shadowing, ×8,000)

Photo. 13.
Precipitation condition
(Cr-shadowing, ×5,000)

Photo. 14.
Crystalline nuclei
(Cr-shadowing, ×5,000)

Photo. 15.
Produced crystals
(Cr-shadowing, ×5,000)

of the precipitated particles L (mμ) is hyperbolic, i.e. $C_0 \times L$ = constant, as indicated in Fig. 2. Accordingly, so long as the particles

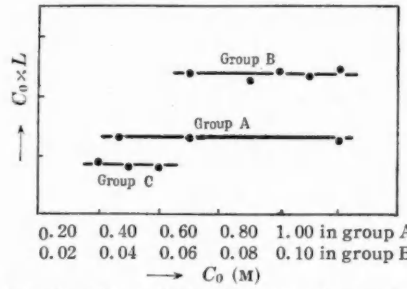

Fig. 2. The relation between the total concentration and the particle size.

of the same shape were concerned, the precipitation law advocated by von Weimarn accorded well with this experiment.

Summary

The shape and the size of barium sulfate precipitate prepared within the range of the total concentrations from 1.0000 to 0.0001 M were observed by an electron microscope. The particles were observed to precipitate in various forms (spherical, spindle, diamond and rectangular) in response to the total concentration of barium sulfate. It was confirmed that the precipitation law advocated by von Weimarn was still substantiated so far as the particles of the same shape were concerned.

The cost of this research has been partly defrayed from the Scientific Research Encouragement Grant of the Ministry of Education, to which the author's thanks are due.

Institute for Chemical Research, Kyoto University, Takatsuki, Osaka

Formation and Aging of Precipitates. II. Electron Microscopic Studies of the Aging of Barium Sulfate Precipitate

By Eiji SUITO and Kazuyoshi TAKIYAMA

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Introduction

The aging of the precipitate is not only significant for the study of its properties, but also interesting from the view-point of the production of powdered materials in the chemical industry. The aging of barium sulfate precipitate has been studied by many investigators by means of various methods. Nowadays, as the electron microscope has made it possible to observe the colloidal dimension, the aging process can be studied in detail.

The authors previously described the shape and size of freshly precipitated barium sulfate[1]. In this paper the aging of the precipitates and the process of the growth of the crystals are described.

I. Aging Process in various Concentrations.

Barium sulfate precipitates produced as described in the previous paper[1] were kept in mother liquor and they were sampled out for electron microscopy at various intervals of time.

1) E. Suito and K. Takiyama, This Bulletin, **27**, 121 (1954).

(*a*) *Crystallization of Gel* In the range of the total concentrations, 1.0~0.5 M, the fresh precipitates were colorless and transparent jellies and seemed to be amorphous. These jellies changed to a white gelatinous mass in a few minutes and settled down after a few days. These sedimented precipitates were composed of spherical particles, which were crystalline, as shown in Photo 2.

(*b*) *Precipitates uniform in Shape and Size* In the range of the total concentrations from 0.10 to 0.01 M the freshly precipitated particles were spindle shaped, cross spindle shaped and diamond shaped and each precipitate had homodisperse or uniform size distribution[1]. In these cases no change of the shape and size was observed for a few months. But the particles precipitated over the range 0.10 to 0.02 M, which had been dendritic and spindle shaped, changed to smooth spindle or hexahedron (rectangle in cross section) shaped ones after about 2 years as shown in Photo 6. Nevertheless, the size of the particles was almost unchanged as shown in Photos 5 and 6. The dendritic particles, which were probably unstable, re-

oriented to ideal crystals, which were rectangular and stable, during the digestion in the mother liquor.

(*c*) *Precipitates not uniform in Shape and Size* At the total concentration of 0.001 M the freshly precipitated particles consisted of two different sizes and shapes, i. e. large diamond shaped particles of about 2 μ and small spindle shaped ones of about 0.2 μ as shown in Photo 8. These smaller ones disappeared after several hours as shown in Photo 9. Two kinds of particles must have appeared by heterogeneous mixing of the reagents. The disappearance of the smaller particles is explained by recrystallization, that is to say, the smaller particles, which were more soluble than the larger ones, dissolved and were deposited on the larger ones.

In the range of the total concentrations below 0.0003 M, the precipitates, which were sampled out immediately after mixing the reagents, consisted of various sizes. In this case the size of the particles changed to uniform as shown in Photo 11 and Ostwald's ripening theory was proved to be valid.

II. Growing Process of Crystal.

In order to study the process of growth of the crystal, the changes of the electric conductivity and the turbidity were measured during the formation of the ideal crystal, whose shape was rectangular.

(*a*) *Change of Conductivity* 10 cc. of barium hydroxide solution and sulfuric acid, whose concentrations were both 0.0021 M, were added simultaneously in to 40 cc. of water. The conductivity of the suspension was measured at ten seconds intervals. The change of the conductivity is indicated by curve 1 in Fig. 1. A rapid change occured about forty seconds after mixing.

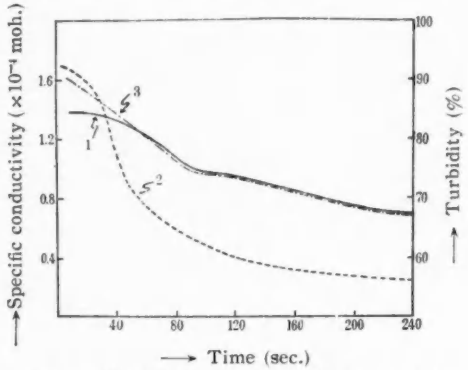

Fig. 1. The change of conductivity and turbidity during the formation of the precipitate.

(*b*) *Change of Turbidity* 2 cc. of barium hydroxide solution and sulfuric acid, whose concentrations were both 0.0021 M, were added into 8 cc. of water. The intensity of the light that passed through the specimen was compared with the intensity of the light that passed through water by means of photocolorimeter. In Fig. 1, curve 2 indicates the intensity of the passed light in percentage. The turbidity changed rapidly about thirty seconds after mixing the reagents.

As indicated in Fig. 1, the curve of the conductivity and the turbidity have a similar form. From these curves, a certain induced period, ten to sixty seconds, is considered to be needed for the formation of the nucleus which grew slowly to the perfect crystal.

(*c*) *Change of Conductivity during the Crystallization in the Presence of Nucleus* 20 cc. of barium hydroxide solution and sulfuric acid, whose concentrations were both 0.0021 M, were added into 40 cc. of the suspension described in (a). The change of the conductivity is indicated by curve 3 in Fig. 1. When the nucleus is present, the crystallization does not require the induced period.

III. Morphology of the Crystals slowly formed and in the Presence of Nucleus.

(*a*) *Crystals slowly formed* The precipitated particles of barium sulfate described above in (II. a) are rectangular as shown in Photo 12, and this shape is ideal for barium sulfate. The ratio of the length of the two edges was almost constant, namely, 2 : 1. Occasionally twin crystals appeared besides these rectangular single crystals. As marked in Photo 12, two twins are observed from different directions by shadowing. As the facet of the twin of orthorhombic crystal is (110), the angle between the two crystals of the twin ought to be about 63°11′, but the angle of the twin shown in Photo 12 is 70° because of the inclination of the crystal to the specimen holder.

(*b*) *Precipitates formed in the Presence of Nucleus* As mentioned above the deposition of the precipitate was promoted by the addition of nucleus. The precipitated particles, which were prepared in the presence of the nucleus as described in (II. c), contained two kinds of rectangular particles, large and small.

The rectangular particles shown in Photo 13 appeared a few minutes after mixing dilute reagents. Before mixing reagents the nuclei, which were diamond shaped as shown in Photo 14, were added to barium hydroxide solution. Immediately after mixing the

reagents, the precipitate shown in Photo 15 appeared. The nuclei grew to angular edged particles and many new rectangular particles appeared. It seems that the nuclei accelerate the separation of the crystals and do not affect the shape of the precipitated particles.

Summary

1. The amorphous precipitate of barium sulfate changed to a crystalline state by aging.
2. The precipitated particles produced in uniform size remained almost unchanged for a few months, but they became perfect for a long period (i. e. a few years).
3. When the particles of two different sizes formed directly after mixing the reagents, the smaller particles went into solution and the larger particles grew at the expense of the small ones.
4. In the case of dilute reagents the rapid change of conductivity was observed in an early stage of the reaction. The nucleus probably formed during this stage.
5. The precipitation was promoted by the nucleus added before the reaction, but the presence of the nucleus did not affect the shape of the precipitated particles.

The authors are grateful to Professor Ishibashi for the use of the facilities of his laboratory in the conductivity and turbidity measurements. The cost of this research has been partly defrayed from the Scientific Research Encouragement Grant of the Ministry of Education, to which the author's thanks are due.

Institute for Chemical Research, Kyoto University, Takatsuki, Osaka

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Surface Chemistry of Synthetic Protein Analogues. III. On the Surface Viscosity of Monolayers of Non-electrolytic Synthetic Polypeptides

By Toshizo ISEMURA and Kozo HAMAGUCHI

(Received October 9, 1953)

Introduction

In the preceding papers of this series,[1),2)] the properties of spread monolayers of some synthetic polypeptides on water investigated by surface pressure measurements were reported in relation to the models of proteins. It was found that poly-DL-α-aminocaproic acid showed very close resemblance of force-area relation to natural proteins such as pepsin and egg albumin among other polypeptides such as poly-DL-α-aminocaprylic acid, poly-DL-α-aminocapric acid and poly-DL-α-aminolauric acid. The latter polypeptides having longer side chains than six carbon atoms in length, gave quite different force-area relation. In F–A curves of these polypeptides, plateau of high compressibility appeared. Poly-γ-methyl-L-glutamate gave condensed film on distilled water. In this case, the polypeptide chain assumed presumably the structure of α-type. This film was expanded on the acidified substrate, and the polypeptide chain may be transformed into β-keratine type. The appearance of the plateau in the F–A curve was attributed to the reorientation of the side chain of the polypeptide. The surface pressure at the plateau depends on temperature and also on the number of carbon atoms in the side chains. From the temperature dependence of the transition pressure and the difference of the areas before and after transformation, the energy needed for reorientation was estimated experimentally.

It is generally accepted that the force-area curves of various natural proteins are not profoundly changed by the species of the proteins. Consequently, it is very difficult to know some characteristics of various proteins from their force-area relations of spread monolayers. On the other hand, it is well-known that the proteins are widely different from each other in their surface viscosity.[3)] Accordingly, the measurements of surface viscosity of the spread monolayers of synthetic polypeptides seemed to be very significant for the comprehension of the natural proteins. In the present paper, the results of the

1) T. Isemura and K. Hamaguchi, This Bulletin, **23**, 40 (1952).
2) T. Isemura and K. Hamaguchi, ibid., **26**, 424 (1953).
3) M. Joly, *J. chim. phys.*, 36, 285 (1939).

measurements of surface viscosity of polypeptide monolayers and also some consideration of the results will be described.

Experimental

Surface viscosity was measured by the damping of the oscillatory motion of rotating disc on the surface of liquid. The method was essentially the same with that adopted by Langmuir and Schaefer[4] and by Joly[5]. The surface pressure was measured simultaneously by the hanging plate method. The moment of inertia of the oscillatory disc (I) was 66.51, and the radius of the disc (R_1) 1.27 cm. The torsion constant of the torsion wire was 42.0. The radius of the film surrounding the oscillatory disc (R_2) was 5.04 cm. The surface viscosity was calculated by the following formula,

$$\eta = \Delta\lambda_{10} \frac{2.3I}{2\tau P}\left(\frac{1}{R_1^2} - \frac{1}{R_2^2}\right)$$

where P is the period of the oscillatory pendulum and $\Delta\lambda_{10}$ is the difference between logarithmic decrements of oscillation both in the presence of film and in the absence of film. The polypeptides examined in the present experiments and their solvents used for the spreading are tabulated in Table I. Side chains and residue weight for amino acid are also shown in the Table.

TABLE I

Polypeptides	Side chains	Residue weight	Solvents
Poly-DL-α-aminocaproic acid	$-(CH_2)_3\cdot CH_3$	113.1	benzene
Poly-DL-α-aminocaprylic acid	$-(CH_2)_5\cdot CH_3$	141.1	benzene
Poly-DL-α-aminocapric acid	$-(CH_2)_7\cdot CH_3$	169.1	benzene
Poly-DL-α-aminolauric acid	$-(CH_2)_9\cdot CH_3$	197.1	benzene
Poly-γ-methyl L-glutamate	$-(CH_2)_2COOCH_3$	143.1	pyridine
Copolypeptide of glycine and alanine			dichloroacetic acid + benzene (1:4)
Poly-γ-benzyl-DL-and L-glutamate	$-(CH_2)COOCH_2C_5H_5$	219.1	chloroform
Amilan		99.1	cresol+benzen (1:3)

Results and Discussion

(I) Viscosity-area Curves of Poly-DL-α-aminocaproic Acid, Poly-DL-α-aminocaprylic acid, Poly-DL-α-aminocapric Acid and Poly-DL-α-aminolauric Acid.

The η–A curves of these polypeptides are shown in Fig. 1. From this figure, it can be

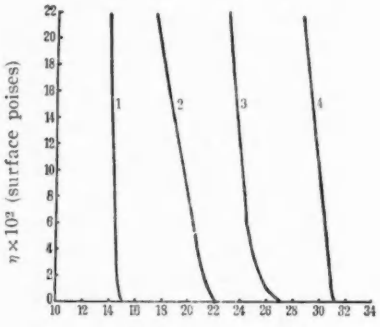


Fig. 1. The surface viscosity-area curves of poly-DL-α-aminocaproic acid (1), poly-DL-α-aminocaprylic acid (2), poly-DL-α-aminocapric acid (3) and poly-DL-α-aminolauric acid (4) (25°C.).

readily seen that the area where surface viscosity was first detected, was related to the side chains. However, the limiting area of the amino-acid residue obtained from the η–A curve for poly-DL-α-aminocaproic acid was 14.7Å^2. This is an area occupied by an amino-acid residue if the polypeptide of β-keratine configuration was packed closely and it also corresponds to the area per residue estimated from X-ray data as already reported in the previous paper.[1] Cumper and Alexander[6] also found 14.7 Å^2 as the limiting area per residue for the monolayer of poly-alanine at liquid/liquid and air/water interfaces and for the monolayer of poly-phenylalanine at air/water interface. However, if the length of the side chain becomes longer than six carbon atoms, as in the case of poly-DL-α-aminocaprylic acid, the limiting area becomes larger with the length of the side chain. Consequently, it seems that the increase of the length of the side chains laid on the surface profoundly affects the increase of surface viscosity. The surface viscosity of these polypeptides with longer side chains reaches considerably high values even under the extremely low surface pressure. So, we can not interpret the η–A curve in relation to the F–A curve of the respective polypeptide. When the surface fluidity, namely, the reciprocal of surface viscosity was plotted as a function of the area per residue, the change of the nature of film could be readily detected from the relation of the fluidity and the area per residue, even at low surface pressure and

4) I. Langmuir and V. J. Schaefer, *J. Am. Chem. Soc.*, **59**, 2400 (1937).
5) M. Joly, *Kolloid-Z.*, **89**, 26 (1939).
6) C. W. N. Cumper and A. E. Alexander, *Trans. Faraday Soc.*, **46**, 235 (1950).

rather high surface viscosity region where any change can hardly be detected from F–A and η–A relations.

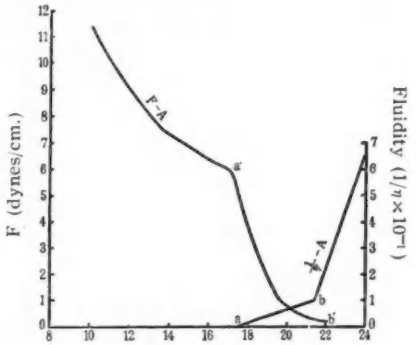


Fig. 2. The force-area and fluidity-area curves of poly-DL-α-aminocaprylic acid (24°C.).

F–A and $1/\eta$–A curve for poly-DL-α-aminocaprylic acid are shown in Fig. 2 and those for poly-DL-α-aminocapric acid in Fig. 3. In these $1/\eta$–A curves, there exist definite kink points b and c. a is the intercept of $1/\eta$–A

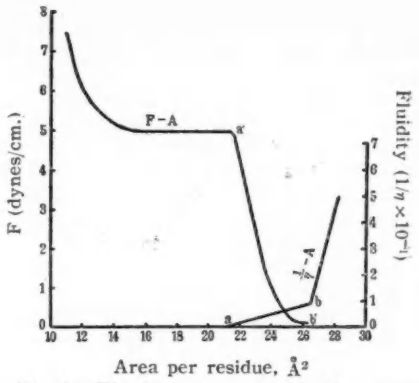


Fig. 3. The force-area and fluidity-area curves of poly-DL-α-aminocapric acid (23°C.).

curve, with area axis extrapolated to zero fluidity. On the other hand, b′ is the area where the surface pressure becomes detectable in the F–A curve and a′ is the area where the plateau begins. These areas are listed in Table II. From the table it will be seen that a is in good agreement with a′ and b with b′.

TABLE II

Polypeptides	Area (Å²/residue) a	a′	b	b′	c	
Poly-DL-α-aminocaprylic acid	17.3	17.2	31.5	21.5	25.3	(24°C.)
Poly-DL-α-aminocapric acid	21.0	22	26.5	24.5	28	(22°C.)
Poly-γ-benzyl-DL-glutamate	19.0	19.5	23.7	24		(9°C.)

(II) Change of Configuration of Poly-γ-methyl-L-glutamate in the Monolayer.

As already reported in the previous paper[1], the monolayer of poly-γ-methyl-L-glutamate behaves differently from other polypeptides, and has a limiting area of 9.8 Å²/residue which was determined by the F–A relation. However, when it was spread on the substrate acidified by formic acid or acetic acid, the monolayer gave the F–A curve analogous to those for other polypeptides with shorter side chain as poly-DL-α-aminocaproic acid and its limiting area per residue was found to be 14.7 Å². The change was interpreted in the light of the results of the infra-red observation of this polypeptide by Ambrose and Hanby[7] and by Bamford, Hanby and Happey[8]. It was concluded that on aqueous substrate the polypeptide assumes the α_{II} configuration proposed by Shimanouchi and Mizushima,[9] and by Ambrase and Hanby[7] independently, and on formic acid or acetic acid solution it turns

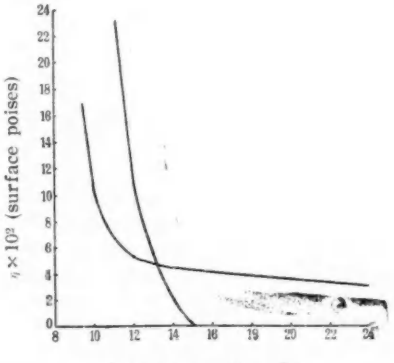


Fig. 4. The surface viscosity-area curves of poly-γ-methyl-L-glutamate. (10°C.): curve I, on distilled water; curve II, on 0.02 N formic acid.

7) E. J. Ambrose and W. E. Hanby, *Nature*, **163**, 483 (1949).
8) C. H. Bamford, W. E. Hanby and F. Happey, *Nature*, **166**, 829 (1950).
9) T. Shimanouchi and S. Mizushima, *Science (Japan)*, **17**, 24, 52 (1947). This Bulletin, **21**, 1 (1948).

to β-keratine type. The difference between both films spread on aqueous and on formic or acetic acid substrate was definitely demonstrated from the results of the surface viscosity measurement. The results are shown in Fig. 4. Curve I in the figure is the η-A curve on the distilled water and Curve II is that obtained on aqueous formic acid substrate (0.02 N). The film, assumed to be as of α-modification on the water surface, was viscous even in low surface concentration which exerts no detectable surface pressure with our surface balance. This is the distinct difference with films of other polypeptides examined. Below the area of 9.8 Å^2/residue, the surface viscosity was rapidly increased with small reduction of area. On the other hand, the viscosity of the film spread on formic acid substrate increases below the area of 14.7 Å^2/residue as other polypeptides of shorter side chains such as poly-DL-norleucine. It is very interesting that this may be the surface chemical indication of the $\alpha \rightarrow \beta$ transformation of poly-γ-methyl-L-glutamate by formic acid.

Recently, our conclusion that the α_{II}-structure proposed by Shimanouchi and Mizushima and by Ambrose and Hanby is plausible for the structure of α-keratine from our result of film area measurement, was criticised by Low[10]. He insisted that our conclusion is invalid because the area was reduced in proportion to the reduction of the length of the main chain, and no consideration for inter-chain packing and orientation was paid. However, in our opinion, when the polypeptide chain was compressed, the polypeptide chain is closely packed so as to orientate the side chain of one side in air and the other in water, irrespective of the structure of the polypeptide in either α- or β-configuration. The thickness of polypeptide chain lying flat should be the same, in the case of both α- and β-structure. This could lead to our conclusion that the area occupied by the closely packed polypeptide chain depends only on the length of the main chain.

(III) Surface Viscosity-area Relation of Copolymer of Glycine and Alanine.

The polypeptides so far investigated were of more than four carbon atoms in length. It is very interesting to investigate how the polypeptides behave at the surface if the polypeptides have no side chains or very short ones. When the polypeptides have long side chains, the coiling of the main chains might be difficult on account of the mutual hindrance of the side chains. In this connection the glycine-alanine copolymer was studied. This copolymer may be easily coiled. It is interesting to compare the behaviour of such a polypeptide with a linear polymer having no side chains such as amilan, on which we will discuss in the later part.

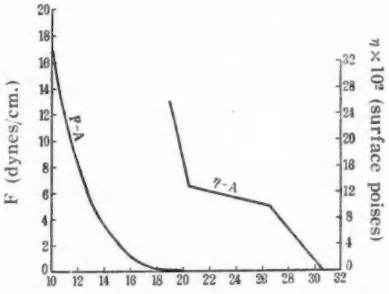


Fig. 5. The surface pressure-area and surface viscosity-area curves of glycine-alanine copolymer (22°C.).

The F–A curve and η–A curve of the glycine-alanine copolymer are shown in Fig. 5. The present investigation of F–A curve, the limiting area per glycine-alanine residue was about 20 Å^2, namely, about 10 Å^2 per amino-acid residue. This fact suggests that this polymer may assume also the structure of folded type as in the case of poly-γ-methyl-L-glutamate. The F–A curve for this copolymer film is, however, different from that for poly-γ-methyl-L-glutamate in its behaviour against the nature of substrate. Although the latter film expands on the acidic substrate considerably, the former film gave the same F–A curve on the acidic substrate as on the distilled water. On the other hand, the surface viscosity of this copolymer film was detected at the area of 30 Å^2 per glycine-alanine residue, namely at the area of 15 Å^2 per amino-acid residue, and at the area of 20 Å^2 per glycine-alanine residue, the surface viscosity was again suddenly increased. This area corresponds to the area from which the surface pressure was suddenly exerted. When the main chain of polypeptide in β-keratine type was packed closely, the residue of amino-acid in polypeptide occupies 15 Å^2 on the surface. On the other hand, the residue of amino-acid occupied 10 Å^2 on the surface, when the main chain of the polypeptide takes the folded structure of α_{II}-type and was packed closely. Accordingly, we might conclude that the copolymer was spread as a film assuming β-keratine type. However, the polypeptide chain will be readily trans-

10) B. W. Low, "The Proteins" ed. by H. Neurath and K. Bailey, Vol. I, Part A, p. 376 (1953).

formed into α-type by slight compression that this transformation cannot be detected by the surface pressure measurement. In the region of this transformation the film may be heterogeneous and the surface viscosity was somewhat fluctuated. From this result mentioned above the polypeptides having very short side chains or none tend to assume readily folded structure. This inference seems plausible from the recent observation of A. Elliott[11] on the infra-red spectrum of poly-DL-alanine. He described in his recent paper, that it is evident that in poly-DL-alanine the equilibrium between α- and β-forms is very nicely balanced, and the transformation from one to the other is readily induced. This conclusion might be applied generally to the polypeptide of very short side chain such as glycine-alanine copolymer. From this viewpoint, our results on the surface viscosity-area relation of this copolymer could be explained successfully.

(IV) The Difference between L-and DL-Polypeptides of γ-Benzyl Glutamate.

For the investigation of the difference between the behaviour of optical active and of racemic polypeptide, the film of poly-γ-benzyl-L-glutamate and of poly-γ-benzyl-DL-glutamate were studied. The F–A and η–A curves of these polypeptides are shown in Fig. 6. On-

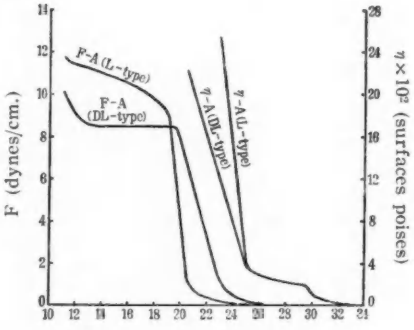


Fig. 6. The surface pressure-area and surface viscosity-area curves of poly-γ-benzyl L- and DL-glutamates (10°C.).

the one hand, F–A curves and η–A curves of these polypeptides showed generally similar trends respectively, and plateaus appeared in the F–A curves for both polypeptides. However, we can notice the following differences by careful inspection of these curves. (1) The limiting area determined from F–A curves were 24 Å/residue for DL-type polypeptide and 21 Å²/residue for L-type polypeptide. (2) The compressibility of the film up to the pressure at which the plateau appears was smaller for L-type polypeptide than for DL-type polypeptide. (3) The F–A curve of poly-γ-benzyl-DL-glutamate was strikingly influenced by temperature as reported in the previous paper.[2] The pressure where the plateau appearing in the F–A curve was decreased with the rise of temperature as in the cases of the films such as poly DL-α-aminolauric acid. On the contrary, in the case of poly-γ-benzyl-L-glutamate, temperature scarcely affected on the F–A relation and the pressure at which the plateau appears, was almost independent of temperature and nearly 8.5 dynes/cm. (4) The area at which the surface viscosity is suddenly increased, was about 25 Å²/residue irrespective of the type of polypeptide. However, the inclination of η–A curve, namely $\partial\eta/\partial A$ was smaller for L-polypeptide than for DL-polypeptide. To clarify the inter-relation between F–A curve and η–A curve, $1/\eta$–A curve was considered. (Fig. 7). a, b, a′ b′,

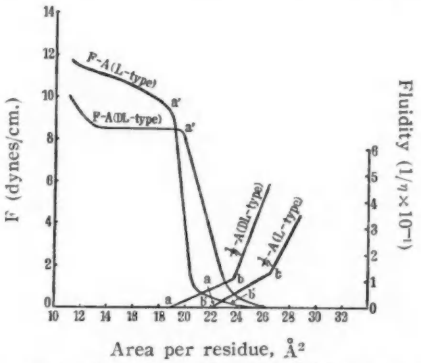


Fig. 7. The force-area and fluidity-area curves of poly-γ-benzyl-DL- and L-glutamates (10°C.).

for L-polypeptide and DL-polypeptide were summarized in Table III. The results shown

TABLE III

Poly-γ-benzyl glutamate	Area (Å²/residue) a	a′	b	b′
L-type	22.3	18.5	26.5	22
DL-type	19.0	19.5	23.7	24

in Table III were obtained as already described, with poly-γ-benyl-DL-glutamate. The area from which the plateau begins to appear, a′, coincides with the area found from extrapolation of $1/\eta$–A curve to $1/\eta=0$. Whereas, with the film of poly-γ-benzyl-L-glutamate, the area from which the surface pressure becomes appreciable, b′ (22 Å²) corresponded to the area found by extrapolation

11) A. Elliott, *Nature*, **170**, 1066 (1952).

of $1/\eta$-A curve to $1/\eta=0$ (21.5Å^2).

From these experimental facts, it can be concluded that the films compressed up to the pressure where the plateau begins to appear, are entirely different for L- and DL-polypeptide, respectively. The arrangement of the L-polypeptide chains is far more closely packed. The film of L-polypeptide in such condition is in a nearly solid state.

(V) The Surface film of Amilan.

F–A curve of the monolayer of amilan was already reported in the previous paper[1]. In F–A curve, a kink point was found at about 32 Å^2/residue. This area is in good agreement with the area occupied by the residue calculated in the basis of the molecular scale model.[9),12)] On the other hand, it was found that some change occurs at the area of 80 Å^2/residue from the sudden change of surface viscosity as shown in Fig. 8. This is

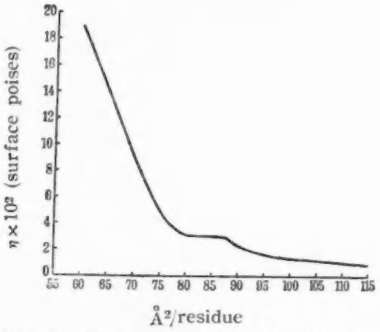


Fig. 8. The surface viscosity-area curve of amilan (22°C.).

entirely different from the films of poly-DL-α-aminocaproic acid and glycine-alanine copolymer. From the surface potential measurement it was found that the potential fluctuated down to the area 80~90 Å^2/residue, below which it changes regularly as reported by Hotta[13] in our Laboratory. Amilan was quite different from the polypeptides films. From this result, our conclusion that amilan is not adequate as the model of protein, was again confirmed.

12) D. J. Crisp, *J. Colloid Sci.*, **1**, 49 (1946).
13) H. Hotta, This Bulletin, **27**, 80 (1954).

Summary

The surface viscosity of the spread monolayers of synthetic polypeptides with non-electrolytic side chains was investigated in relation to the surface area and to the surface pressure. If the length of a side chain becomes longer than six carbon atoms, the limiting area becomes larger with the length of the side chain. Polypeptide with no side chains or very short ones such as glycine-alanine copolymer might be changed to α-configuration from "extended" β-configuration merely by compression. The ease of transition from one configuration to another corresponds to the discovery by Elliott in bulk solution with poly-alanine. $\alpha_{II} \rightarrow \beta$ transformation of poly-γ-methyl-L-glutamate which had been reported in the previous paper, was observed also by the surface viscosity measurements. The difference of the nature of films of optical active and of racemic polypeptide was investigated. The polypeptide consisting of single optical isomeride was able to be more closely packed in the film than that of racemic. Our discovery by surface pressure measurement that the polymer of ϵ-aminocaproic acid, namely, amilan is not adequate as the model of protein, was again confirmed from the study of surface viscosity.

The authors wish to express their sincere thanks to Dr. H. Tani and Mr. H. Yuki in the Faculty of Science, Osaka University and to Dr. J. Noguchi at Kanazawa University who gave them the valuable samples of synthetic polypeptides. A part of the expense for the experiment has been defrayed from a grant given by the Ministry of Education, to whom the authors' thanks are due.

The Institute of Scientific and Industrial Research.
Osaka University, Sakai, Osaka

The Condensation of Benzaldehyde with Methyl Ethyl Ketone by Aqueous Sodium Hydroxide

By Hiroshi MIDORIKAWA

(Received November 4, 1953)

Harries and Müller[1] demonstrated that, when aqueous sodium hydroxide was employed as the condensing agent, benzaldehyde condensed with methyl ethyl ketone at the α-methyl group of the ketone at ordinary temperature, forming 1-phenyl-1-penten-3-one, and, when hydrogen chloride was employed as the condensing agent, benzaldehyde reacted with methyl ethyl ketone at its α-methylene group, giving 3-methyl-4-phenyl-3-buten-2-one.

In the preceding report[2], it was indicated that furfural condensed with methyl ethyl ketone chiefly by aqueuos sodium hydroxide at its methylene group at the lowered reaction temperature 0~5°, giving the chief product 4-(2-furyl)-3-methyl-4-butanol-2-one, whereas furfural condensed with the ketone chiefly at its α-methyl group at the elevated reaction temperature 60~65°, giving 1-(2-furyl)-1-penten-3-one.

In the present experiment, the condensation of benzaldehyde with methyl ethyl ketone by aqueous sodium hydroxide at lowered and elevated reaction temperatures was studied in order to compare it with the result of furfural in the preceding report[2].

At the elevated reaction temperature 60~65°, the condensation of benzaldehyde with methyl ethyl ketone gave only 1-phenyl-1-penten-3-one (I) as illustrated below, since this condensation product afforded an oxime melting at 86~87° which was identical with that of 1-phenyl-1-penten-3-one obtained by Harries and Müller.[1] The semicarbazone of this ketone melted at 181~182°.

At the lowered reaction temperature 3~5°, benzaldehyde and methyl ethyl ketone underwent aldol condensation by sodium hydroxide, giving a mixture of 3-methyl-4-phenyl-4-butanol-2-one (II) and 1-phenyl-1-pentanol-3-one (III), as illustrated below. The mixture of these condensation products gave no semicarbazone, but, after the dehydration with acetic anhydride, gave a mixture of a semicarbazone melting at 218~219° in a larger proportion and the semicarbazone (m.p. 181~182°) of 1-phenyl-1-penten-3-one in a smaller proportion. The semicarbazone melting at 218~219° was identified with that of 3-methyl-4-phenyl-3-buten-2-one obtained by condensing benzaldehyde with methyl ethyl ketone by hydrogen chloride. Consequently, it was confirmed that the condensation products at the reaction temperature 3~5° were a larger amount of 3-methyl-4-phenyl-4-butanol-2-one (II) and a smaller amount of 1-phenyl-1-pentanol-3-one (III), and, on the dehydration with acetic anhydride, gave the corresponding unsaturated ketones, 3-methyl-4-phenyl-3-buten-2-one (IV) and 1-phenyl-1-penten-3-one (I).

Furthermore, 3-methyl-4-phenyl-3-buten-2-one was oxidized by sodium hypochlorite to α-methylcinnamic acid (V), while 1-phenyl-1-penten-3-one (I) was not acted upon by this oxidizing agent.

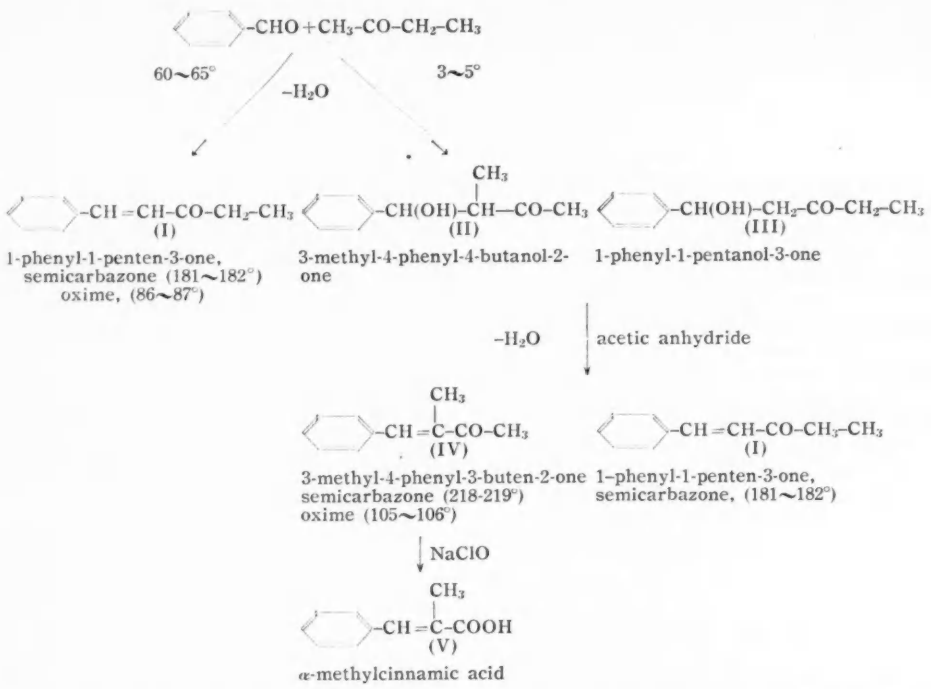
The overall reactions are illustrated by the following formulation.

3-Methyl-4-phenyl-3-buten-2-one (IV) and 1-phenyl-1-penten-3-one (I) obtained here gave respective 2,4-dinitrophenylhydrazones. It was of interest that the mixture of the aldol condensation products at the reaction temperature 3~5°, on the reaction with 2,4-dinitrophenylhydrazine in methanolic sulfuric acid, gave the 2,4-dinitrophenylhydrazones of 1-phenyl-1-penten-3-one (I) and benzaldehyde, but no 2,4-dinitrophenylhydrazone of 3-methyl-4-phenyl-3-buten-2-one (IV). This result appeared to indicate that, under such a reaction condition, 1-phenyl-1-pentanol-3-one (III) gave 2,4-dinitrophenylhydrazone of 1-phenyl-1-penten-3-one (I) with simultaneous dehydration, and 3-methyl-4-phenyl-4-butanol-2-one (II) initially dissociated to methyl ethyl ketone and benzaldehyde, which subsequently gave its 2,4-dinitrophenylhydrazone.

Experimental

Condensation at Reaction Temperature 3~5° Into a stirred suspension of benzaldehyde (20 g.) and methyl ethyl ketone (40 g.) in water (300 cc.) was at once introduced 10% aqueous sodium hydroxide (15 cc.) at 3°. The reaction was complete after prolonged stirring for 6 hrs. at 3~5°. The reaction mixture was neutralized with dilute sulfuric acid, the oily layer separated and the aqueous solution extracted twice with ether. The oily layer and the ether extract were combined and dried over anhydrous sodium sul-

1) C. Harries and G. H. Müller, *Ber.*, **35**, 966 (1902).
2) H. Midorikawa, This Bulletin, **26**, 460 (1953).



fate. Fractionation of the ethereal solution gave a pale yellow liquid (25 g.), b.p. 122~129°/6 mm. This fraction was considered to consist of 3-methyl-4-phenyl-4-butanol-2-one (II) in a larger proportion and 1-phenyl-1-pentanol-3-one (III) in a smaller proportion. Calcd. for $C_{11}H_{14}O_2$: C, 74.11 H, 7.92; Found: C, 72.22, H, 7.67%.

This analysis appeared to show that this fraction contains a small quantity of the dehydrated ketones $C_{11}H_{12}O$, but the fraction gave no semicarbazone. From this fraction were obtained two 2,4-dinitrophenylhydrazones in equal proportions, which were readily separable from each other by the difference of the solubility in nitrobenzene. The more soluble one crystallised in red needles, m.p. 212~213°, undepressed on admixture with 2,4-dinitrophenylhydrazone of 1-phenyl-1-penten-3-one (I) as indicated below. The less soluble one formed orange prisms melting at 235~236°, undepressed on admixture with benzaldehyde 2,4-dinitrophenylhydrazone.

Dehydration of the Condensation Product at the Reaction Temperature 3~5C° The foregoing aldol condensation product (5 g.) at the reaction temperature 3~5° was refluxed with acetic anhydride (15 g.) for 16 hrs. Fractionation of the reaction mixture gave a pale yellow oil (4 g.), b.p. 112~114°/6 mm.

This oil (0.5 g.) was suspended in an aqueous semicarbazide-sodium acetate solution, and methanol added until a clear solution was obtained. The solution, after heating on the water-bath for a short time and standing for 3 hrs., gave colourless crystals (0.4 g.), which was recrystallised from methanol as plates, m.p. 218~219°, undepressed on admixture with the semicarbazone of 3-methyl-4-phenyl-3-buten-2-one (IV) indicated below. The filtrate on standing overnight gave colourless crystals (0.1 g.), which were recrystallised twice from methanol in needles, m.p. 181~182°. This specimen was identical with the semicarbazone of 1-phenyl-1-penten-3-one (I).

The oil (1 g.), above mentioned was suspended in an aqueous sodium hypochlorite solution[2] (8 cc.) at ordinary temperature with occasional shaking for 2 days. The reaction mixture was freed of oily matter by extraction with ether, and acidified with dilute hydrochloric acid to yield crystals (0.3 g.) on cooling, which were recrystallised from water as colourless prisms, m.p. 77~78°. This specimen was identified with α-methylcinnamic acid (V); lit[3]., m.p. 78°. Calcd. for $C_{10}H_{10}O_2$: C, 74.04, H, 6.22%; Found: C, 73.96, H, 6.11%.

Cndensation at the Reaction Temperature 60~65° Into a stirred suspension of benzaldehyde (15 g.) and methyl ethyl ketone (30 g.) in water (200 cc.) was at once introduced 10% aqueous sodium hydroxide (7 cc.) at about 60°. After prolonged stirring for 3 hrs. at 60~65°, the reaction was over. The reaction mixture was worked up as described above. Fractionation of the ether solution, after drying over calcium chloride, gave a pale yellow oil (19 g.), b.p. 117~118°/6 mm., which solidified at ordinary temperature. This fraction was composed of 1-phenyl-1-penten-3-one (I). Calcd. for $C_{11}H_{12}O$: C, 82.45 H, 7.55%; Found:

C, 82.29 H, 7.70%.

This fraction gave the oxime melting at 86~87°, which was identical with the oxime (m.p. 85~86°) of 1-phenyl-1-penten-3-one (I) obtained by Harries and Müller[1]. Its semicarbazone formed colourless needle crystals melting at 181~182° (lit[4]., m.p. 173°), and its 2,4-dinitrophenylhydrazone, carmine rhombic crystals, melting at 212~213° on crystallisation from pyridine. Calcd. for $C_{17}H_{16}O_4N_4$: C, 59.97, H, 4.74, N, 16.46%; Found: C, 59.78, H, 4.59, N, 16.50%.

3-Methyl-4-phenyl-3-buten-2-one (IV) was synthesised from benzaldehyde and methyl ethyl ketone by the use of hydrogen chloride as the condensing agent, as reported by Harries and Müller[1]. This ketone gave the oxime melting at 105~106° (lit[1]., m.p. 103~104°), the semicarbazone melting at 218~219° (lit[4]., m.p. 204°) and a 2,4-dinitrophenylhydrazone, red needles, melting at 199~200°. Calcd. for $C_{17}H_{16}O_4N_4$: C, 59.97, H, 4.74, N, 16.46%; Found: C, 59.52, H, 4.56, N, 16.51%.

3) R. Stoermer and R. Wehlu: *Ber.*, **35**, 3552 (1902).
4) C. V. Gheroghiu and B. Arwentiew: *Bull. Soc. Chim.*, **47**, 195 (1930).

Summary

In the condensation of benzaldehyde with methyl ethyl ketone by aqueous sodium hydroxide, the lowered reaction temperature (3~5°) favored the aldol condensation at the α-methylene group of the ketone as in the condensation of furfural with the ketone[2]. On the other hand, the elevated reaction temperature (60~65°) conducted exclusively the condensation at the α-methyl group of the ketone, giving 1-phenyl-1-penten-3-one (I).

3-Methyl-4-phenyl-4-butanol-2-one (II), obtained by the aldol condensation at the lowered reaction temperature (3~5°), was dehydrated with acetic anhydride to 3-methyl-4-phenyl-3-buten-2-one (IV), which was oxidized by sodium hypochlorite to afford α-methylcinnamic acid (V).

The author expresses his sincere thanks for Dr. T. Hayashi for his kind advice.

Scientific Research Institute, Komagome, Bunkyo-ku, Tokyo

Visco-Elasticity Measurement by the Torsional Rheometer. Simple Treatment by the Application of the Four-Terminal Network

By Tsurutaro NAKAGAWA

(Received November 10, 1953)

Introduction

Some polymer and colloidal solutions, in contrast to ordinary liquids of low molecular weight, have been known to show elastic nature besides viscosity, and rheological peculiarities of these "elastic liquids"—e. g. "Fliesselastizität" (H. Freundlich, 1932), "structural viscosity" (W. Philippoff, 1935), "thread-forming ability" (H. Erbring, 1936), "Weissenberg effect" (K. Weissenberg, 1947) etc. have been studied by various workers. As it has recently become desirable to analyse such rheological behaviors of those solutions, various rheometers or elastoviscometers suitable for the measurement of their visco-elastic properties have been proposed, and among them it is thought that the rheometers in which the most rigorous treatment has been given are those of coaxial-cylinder type which provide a means of maintaining a liquid in a state of torsional oscillation in a narrow annular gap between two vertical coaxial cylinders.

In this paper, the author gives a simple general view of the rheometers of this type by the application of the four-terminal electrical network theory. The treatment by the four-terminal network is better than that by the ordinary two-terminal network from the view-point that the former can include all modifications of the rheometer by a single four-terminal circuit diagram.

It goes without saying that the treatment presented here is only approximate; the inertia of the sample liquid is neglected here. This approximation, however, is satisfactory in the measurement at very low frequencies.*

Survey of the Four-Terminal Network Theory

An electrical network which has two input and two output terminals is called a four-terminal network.

When the generalized Kirchhoff's law is applied to the four-terminal network N (Fig. 1.), the fundamental equation of the network is derived in terms of the "four-terminal

* T. Nakagawa, Third Rheological Meeting, Japan, 1953.

constants" A, B, C and D as

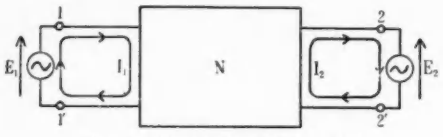


Fig. 1. Four-terminal network.

$$E_1 = AE_2 + BI_2 \tag{1a}$$

$$I_1 = CE_2 + DI_2 \tag{1b}$$

or, according to the matrix expression,

$$\begin{pmatrix} E_1 \\ I_1 \end{pmatrix} = \begin{pmatrix} A & B \\ C & D \end{pmatrix} \begin{pmatrix} E_2 \\ I_2 \end{pmatrix} \tag{2}$$

where E_1 and I_1 are the input voltage and the input current respectively; E_2 and I_2 are the quantities relating to the output. The four-terminal constants A B C D are shown to satisfy the next relation.

$$\begin{vmatrix} A & B \\ C & D \end{vmatrix} = AD - BC = 1 \tag{3}$$

According to the theory, the four-terminal constants of a circuit which has a single impedance Z as shown in Fig. 2 are

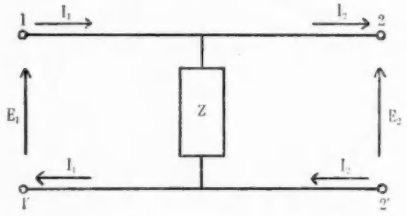


Fig. 2. Single-impedance network (I).

$$\begin{pmatrix} A & B \\ C & D \end{pmatrix} = \begin{pmatrix} 1 & 0 \\ 1/Z & 1 \end{pmatrix} \tag{4}$$

and for a circuit of Fig. 3, they are

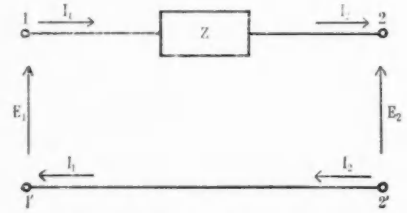


Fig. 3. Single-impedance network (II).

$$\begin{pmatrix} A & B \\ C & D \end{pmatrix} = \begin{pmatrix} 1 & Z \\ 0 & 1 \end{pmatrix} \tag{5}$$

When a four-terminal circuit N_2 is connected tandem to the right hand side of a four-terminal circuit N_1, a new four-terminal circuit N is constructed and its four-terminal constants A B C D are obtained from the product of two matrices

$$\begin{pmatrix} A & B \\ C & D \end{pmatrix} = \begin{pmatrix} A' & B' \\ C' & D' \end{pmatrix} \begin{pmatrix} A'' & B'' \\ C'' & D'' \end{pmatrix} = \begin{pmatrix} A'A''+B'C'' & A'B''+B'D'' \\ C'A''+D'C'' & C'B''+D'D'' \end{pmatrix} \tag{6}$$

where A' B' C' D' and A'' B'' C'' D'' are four-terminal constants of the network N_1 and N_2 respectively (Fig. 4.).

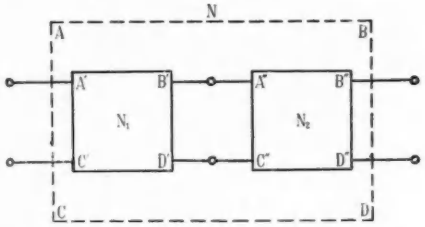


Fig. 4. Tandem connection of two four-terminal networks.

From the above-stated, the four-terminal constants of a π-type network which is composed of three impedances as shown in Fig. 5 are easily obtained as follows by the cascade connection of three circuits illustrated in Fig. 2 and 3.

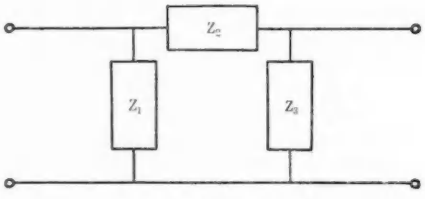


Fig. 5. π-type network.

$$\begin{pmatrix} A & B \\ C & D \end{pmatrix} = \begin{pmatrix} 1 & 0 \\ 1/Z_1 & 1 \end{pmatrix} \begin{pmatrix} 1 & Z_2 \\ 0 & 1 \end{pmatrix} \begin{pmatrix} 1 & 0 \\ 1/Z_3 & 1 \end{pmatrix} = \begin{pmatrix} 1+Z_2/Z_3 & Z_2 \\ (Z_1+Z_2+Z_3)/(Z_1Z_3) & 1+Z_2/Z_1 \end{pmatrix} \tag{7}$$

The Torsionally Oscillating Rheometer and the Four-Terminal Circuit

In this rheometer, a cylinder of radius r_1 is suspended coaxially to a depth l in a liquid contained in a cup of radius r_2. The rheometer of this type is used in two modi-

fications. In one,[1,1',2,3,3'] the external cup is caused to oscillate through a small fixed angular amplitude Θ_0, while the top end of the suspension wire is fixed; in the other[1',4,5,3], the top end of the suspension wire is put into the torsional oscillation $\Theta=\Theta_0 e^{j\omega t}$, the cup being fixed. In both cases the rheological properties of the sample liquid are known from the analysis of the motion of the internal cylinder relative to that of the external cup or to that of the top of the suspension wire.

When the experiment is carried out at very low frequencies (period $T=2\pi/\omega$, greater than several seconds) a simple approximate treatment seems to be permissible*. Here the inertia of the sample is assumed to be negligible and to have no effect on the motion of the inner cylinder. And moreover, the next two relations, in which viscosity η and rigidity G are related to the resistance R and the stiffness E by a simple shape factor K_0, are assumed to hold. Of the reason for employing this shape factor reference will be made in the later section on the rotational viscometer and Schwedoff's apparatus.

$$\eta=\frac{R}{4\pi l}\left(\frac{1}{r_1^2}-\frac{1}{r_2^2}\right)\equiv K_0 R \quad \text{poises} \qquad (8)$$

$$G=\frac{E}{4\pi l}\left(\frac{1}{r_1^2}-\frac{1}{r_2^2}\right)\equiv K_0 E \quad \text{dyn./cm}^2. \qquad (9)$$

Analogous Four-Terminal Network.—A simple consideration enables us to construct an analogous four-terminal network a in Fig. 6 corresponding to our rheometer where the electro-mechanical correspondence is as is listed in Table 1. Fig. 6 is a π-type

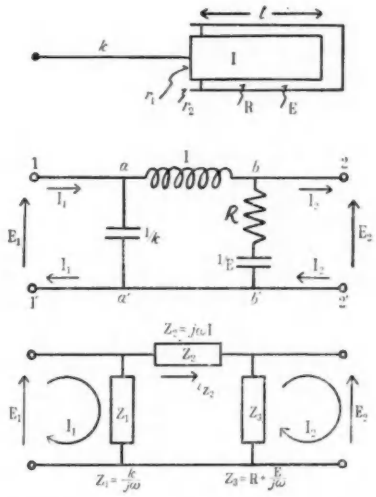


Fig. 6. Torsionally oscillating rheometer and the analogous four-terminal network.

TABLE I

ELECTRO-MECHANICAL CORRESPONDENCE

Mechanical System		Electrical System
k :	Torsion constant of suspension wire	Reciprocal capacitance
I :	Moment of inertia of inner cylinder	Inductance
R :	Viscous resistance of sample	Resistance
E :	Stiffness of sample	Reciprocal capacitance
$\dot{\theta}$:	Velocity	i : Current
θ :	Displacement	Q : Charge

circuit which was stated above, and since

$$\left.\begin{aligned} Z_1&=\frac{k}{j\omega}\\ Z_2&=j\omega I\\ Z_3&=R+\frac{E}{j\omega}\end{aligned}\right\} \qquad (10)$$

the four-terminal constants $A\ B\ C\ D$ are calculated by Eq. 7; and, for example,

$$C=(Z_1+Z_2+Z_3)/(Z_1Z_3)=\frac{(j\omega R-\omega^2 I+k+E)}{k\left(R+\frac{E}{j\omega}\right)} \qquad (11)$$

1) J. R. Van Wazer and H. Goldberg, *J. Appl. Phys.*, **18**, 207 (1947).
1') H. Goldberg and O. Sandvik, *Anal. Chem.*, **19**, 123 (1947).
2) J. R. Van Wazer, *J. Colloid Sci.*, **2**, 223 (1947).
3) H. Markovitz et al., *Rev. Sci. Instr.*, **23**, 430 (1952); H. Markovitz, *J. Appl. Phys.*, **23**, 1070 (1952).
3') J. G. Oldroyd et al., *Proc. Phys. Soc.*, B, **64**, 44 (1951); J. G. Oldroyd, *Quart. Journ. Mech. and Applied Math.* **4**, Pt. 3, 271 (1951).
4) T. Nakagawa, *J. Chem. Soc. Japan*, **72**, 759 (1951) (in Japanese).
5) T. Nakagawa, This Bulletin **24**, 191 (1951).
6) T. Nakagawa, ibid., **25**, 53 (1952).
* The exact treatment of the torsionally oscillating rheometer taking account of the inertia of the sample has recently been done by various authors; so for the cup-drive system, see for example, J. G. Oldroyd,[3'] A. A. K. Ibrahim and A. M. Kabiel, *J. Appl. Phys.*, **23**, 754 (1952), and H. Markovitz[3]; for the top-drive system, see S. Oka, *Bull, Kobayashi Inst. of Phys. Res.*, **3**, 9 and 17 (1953) (in Japanese).

where $j=\sqrt{-1}$, and ω is 2π times the frequency ν ($\omega=2\pi\nu$).

The angular velocity $\dot{\theta}$ of the inner cylinder corresponds to the current i_{Z2} which flows through the inductance I, and to know the angular displacement of the inner bob it is enough to compute the charge Q_{Z2}

$$Q_{Z2}=\frac{i_{Z2}}{j\omega} \tag{12}$$

(1) **Top-Drive System.**—First is discussed the case in which the cup is fixed and the top end of the suspension wire is subjected to oscillational displacement

$$\Theta=\Theta_0 e^{j\omega t}$$

This situation is electrically as follows (Fig. 7). The input current at the terminal 1—1′ is

$$I_1=j\omega\Theta_0 e^{j\omega t},$$

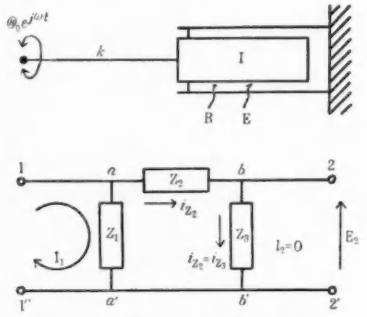


Fig. 7. Top-drive rheometer.

and the velocity of the cup is zero, that is, the terminal 2—2′ is opened

$$I_2=0$$

From Eq. (1b) of the four-terminal equation

$$E_2=\frac{I_1}{C}$$

The angular velocity of the inner cylinder $\dot{\theta}$ corresponds to i_{Z2}, and

$$i_{Z2}=i_{Z3}=\frac{E_2}{Z_3}=\frac{I_1}{CZ_3}$$

$$=\frac{k\Theta_0 e^{j\omega t}}{R+j\left(\omega I-\dfrac{k+E}{\omega}\right)}$$

So that

$$\theta=\frac{\dot{\theta}}{j\omega}=\frac{k\Theta_0 e^{j\omega t}}{[(k+E)-\omega^2 I]+j\omega R}$$

$$\therefore\ \theta=\frac{k\Theta_0}{\sqrt{(k+E-\omega^2 I)^2+\omega^2 R^2}}e^{j(\omega t-\phi)}\equiv Ae^{j(\omega t-\phi)}$$

where $$\tan\phi=\frac{\omega R}{(k+E-\omega^2 I)} \tag{13}$$

This result of course agrees with that obtained by the direct solution of the equation of motion of the inner cylinder

$$I\ddot{\theta}=k(\Theta-\theta)-R\dot{\theta}-E\theta$$

If m, the amplitude ratio A/Θ_0 and ϕ, the phase angle are observed, R and E are known from Eq. 13 or from

$$\begin{cases} R=\dfrac{kT\sin\phi}{2\pi m} \\ E=k\left(\dfrac{\cos\phi}{m}-1\right)+\dfrac{4\pi^2 I}{T^2} \end{cases} \tag{14}$$

where $T=2\pi/\omega$, and consequently η and G can be calculated from Eqs. 8 and 9. Or the observation of the amplitude resonance enables us to calculate η and G[4,11],[**] from

$$\begin{cases} \omega_{res}=2\pi\nu_{res}=\sqrt{n_0^2-2\epsilon^2} \\ A_{res}=L/\sqrt{4\epsilon^4+4\epsilon^2\omega^2_{res}} \end{cases}$$

where ν_{res} and A_{res} are the resonance frequency and the resonance amplitude respectively, and

$$2\epsilon=R/I,\quad n_0^2=(k+E)/I,\quad L=k\Theta_0/I.$$

(2) **Cup-Drive System.**—In this case the external cup is put into sinusoidal oscillation, and the top end of the suspension wire is fixed (Fig. 8.). This condition corresponds electrically to the case in which, contrary to that of the top-drive system,

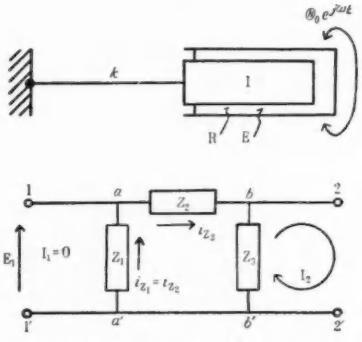


Fig. 8. Cup-drive rheometer.

$$I_1=0$$
$$I_2=j\omega\Theta_0 e^{j\omega t}$$

[**] The resonance method starting from Eq. (13) which implies the neglect of the inertia of the sample, however, seems to be doubtful, for in this case the observation is ordinarily made at the frequencies several cycles per second or more, and then the inertia of the liquid can not be neglected. With the phase angle method, on the other hand, very low frequencies can be adopted and then Eq. 13 is satisfactory.

and the four-terminal equation is

$$E_1 = AE_2 + BI_2 \tag{1a}$$

$$I_1 = 0 = CE_2 + DI_2 \tag{1b}$$

From (1a), (1b) and (3)

$$E_1 = \left(B - \frac{AD}{C}\right) I_2 = \frac{(BC-AD)}{C} I_2 = \frac{-1}{C} I_2$$

$$= -\frac{Z_1 Z_3}{(Z_1+Z_2+Z_3)} \cdot j\omega\Theta_0 e^{j\omega t}$$

$\dot{\theta}$ corresponds to i_{Z_2}, and

$$i_{Z_2} = i_{Z_1} = -\frac{E_1}{Z_1}$$

So that

$$\theta = \int \dot{\theta} dt = \frac{\dot{\theta}}{j\omega} = \frac{(E+j\omega R)\Theta_0}{[(k+E-\omega^2 I)+j\omega R]} e^{j\omega t}$$

or

$$\theta = \frac{\sqrt{E^2+\omega^2R^2} \cdot \Theta_0}{\sqrt{(k+E-\omega^2 I)^2+\omega^2 R^2}} e^{j(\omega t-\phi)} \tag{15}$$

$$\tan\phi = \frac{\omega R(\omega^2 I - k)}{E(k+E-\omega^2 I)+\omega^2 R^2}$$

This is somewhat complicated in comparison with Eq. 13. It is not possible to obtain a relation as simple as Eq. 14 for the calculation of R and E from the observed m and ϕ***.

(3) **Impedance-Less Suspension** In the rheometer which was used by J. R. Van Wazer and H. Goldberg[1] the internal cylinder is suspended from a thin thread whose mechanical loss and elastance are both assumed to be negligible in comparison with those of the liquid under study. The external cup is set into oscillation. This situation corresponds to Fig. 9 in which the terminals a and a' are short-circuited and

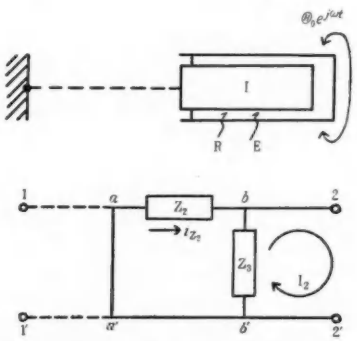


Fig. 9. Impedance-less suspension rheometer.

*** In this case the rigorous analysis[2,2'] is rather convenient to use.

$$Z_1 = \frac{k}{j\omega} = 0$$

When we put $k=0$ in Eq. 15, motion of the internal cylinder in the case of the impedance-less suspension is obtained as

$$\theta = \frac{\sqrt{E^2+\omega^2R^2} \cdot \Theta_0}{\sqrt{(E-\omega^2 I)^2+\omega^2 R^2}} e^{j(\omega t-\phi)} \equiv A_0 e^{j(\omega t-\phi)}$$

$$\tan\phi = \frac{\omega^3 RI}{E(E-\omega^2 I)+\omega^2 R^2}$$

If we differentiate A_0 and set $\partial A_0/\partial\omega$ equal to zero, the condition for a maximum, or for the amplitude resonance, is fulfilled and we find that

$$\omega^2_{res} = \frac{-n_s^4 + n_s^4 \cdot \sqrt{1+8\varepsilon^2/n_s^2}}{4\varepsilon^2}$$

at resonance, where $2\varepsilon = R/I$ and $n_s^2 = E/I$. When $\varepsilon^2 \ll n_s^2$, or when the elastic nature is very strong in the liquid under study,

$$\omega^2_{res} = \frac{-n_s^4 + n_s^4(1+4\varepsilon^2/n_s^2)}{4\varepsilon^2} = n_s^2 = \frac{E}{I}$$

So that it is possible to know the elastic constant of an elastic liquid approximately from

$$G = \frac{I}{4\pi l}\left(\frac{1}{r_1^2} - \frac{1}{r_2^2}\right)\omega^2_{res}$$

(It is of course possible to calculate the true shear modulus and the damping viscosity by the appropriate correctional procedure[1].)

The resonance method, however, as was mentioned previously, seems to be incorrect from the point that the inertia of the sample can not be neglected in the frequency range usually adopted.

(4) **Rotational Viscometer and Schwedoff Apparatus** Apart from the oscillating devices, two simple rheometers will be mentioned; one of them is the rotational viscometer and the other is the apparatus which was used by Th. Schwedoff[7] and others[8] to measure the shear modulus of gel-like matter.

Rotational Viscometer. — In the ordinary type rotational viscometer (Couette-Hatschek apparatus) the external cylinder rotates with a constant angular velocity Ω, while the top end of the suspension wire is kept in position. The stationary state is reached after the inner cylinder is deflected to a certain extent θ.

The electrical analog is illustrated in Fig. 10; the input terminals $1-1'$ are opened and the output direct current $I_2 = \Omega$ (D.C.). In

7) Th. Schwedoff, *J. de Phys.*, [2] **8**, 341 (1889).
8) E. Hatschek and R. S. Jane, *Koll. Z.*, **39**, 300 (1926); H. J. Poole, *Trans. Farad. Soc.*, **22**, 82 (1926).

the stationary state the inductance I is inactive because no current flows in it, and counter-electromotive force at the resistor part balances with that of the capacitor

$$R\Omega = \frac{\theta}{1/k}$$

or

$$R\Omega = k\theta$$

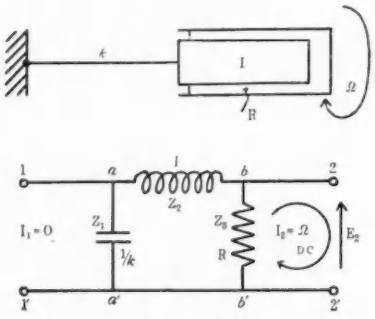


Fig. 10. Rotational viscometer.

The well-known Couette-Hatschek formula of the rotational viscometer is

$$\frac{4\pi l}{\left(\frac{1}{r_1^2}-\frac{1}{r_2^2}\right)}\eta\Omega = k\theta$$

and then

$$\eta = \frac{R}{4\pi l}\left(\frac{1}{r_1^2}-\frac{1}{r_2^2}\right) \equiv K_0 R \qquad (8)$$

It has simply been assumed in the present discussion that the relation 8 holds in the oscillatory case too.

Schwedoff Apparatus.—In the Schwedoff method for measuring the elasticity of typical elastic gels—e.g. gelatin gel, agar-agar gel and so on, the top end of the suspension wire is twisted to an angle θ_1 and the equilibrium deflection θ_2 of the internal cylinder is observed.

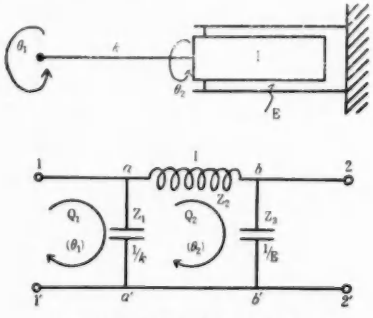


Fig. 11. Schwedoff apparatus.

The situation is that at the equilibrium the inductance is inactive and the voltage Q (charge)/C (capacitance) of the one capacitor is equal to that of the other (cf. Fig. 11 and Table I).

$$\frac{(\theta_1-\theta_2)}{1/k} = \frac{\theta_2}{1/E}$$

or

$$E = k\frac{(\theta_1-\theta_2)}{\theta_2}$$

The exact formula derived by Schwedoff is

$$G = \frac{k}{4\pi l}\left(\frac{1}{r_1^2}-\frac{1}{r_2^2}\right)\cdot\frac{(\theta_1-\theta_2)}{\theta_2}$$

Then

$$G = \frac{E}{4\pi l}\left(\frac{1}{r_1^2}-\frac{1}{r_2^2}\right) \equiv K_0 E \qquad (9)$$

The author has extended this shape factor K_0 to the case of the dynamic elasticity throughout the discussion.

As to the time effect of the elastic deformation of gels, (a) the elastic after-effect (retarded elasticity or parallel visco-elasticity) is described by a resistor element inserted in series to the capacitor of Z_3, and (b) flow (relaxed elasticity or series visco-elasticity) is analogized by a leakage resistance inserted in parallel in Z_3.

(5). More Complicated Cases.—When the cup and the upper end of the wire are both driven, the general case must be solved in

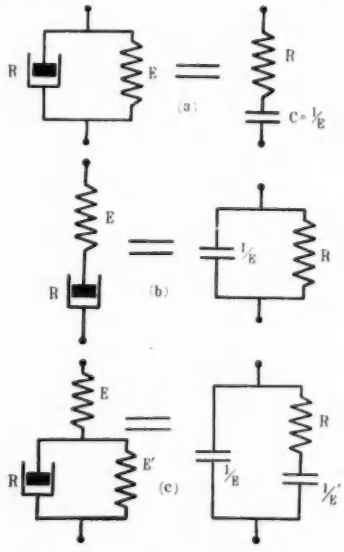


Fig. 12. Mechanical models and corresponding networks.

which $I_1 \neq 0$, $I_2 \neq 0$ and they are in some phase difference.

Throughout the discussion the $R-C$ series circuit was assumed as to the components of Z_3, corresponding to the parallel mechanical model (Voigt model) as is shown in Fig. 12 a, in which $Z_3 = R + E/(j\omega)$. If necessary, however, other impedance functions may be adopted—e.g. $R-C$ parallel circuit corresponding to Maxwell model (Fig. 12 b), or three-element model (Fig. 12 c) in which

$$Z_3 = \frac{1}{\frac{1}{E/(j\omega)} + \frac{1}{R+E'/(j\omega)}}$$

Summary

(1) The four-terminal electrical network is shown to be useful in the schematic representation of various mechanical systems.

(2) A simple review on various types of torsionally oscillating rheometers is given according to the theory of four-terminal networks.

(3) It is shown that complicated viscoelastic systems are easily solved so far as their formalistic treatment is concerned.

The author hereby expresses his thanks to Prof. H. Akamatsu for his interest and the support given to him in this study.

Department of Chemistry, Faculty of Science, Tokyo University, Tokyo

Radiochemical Studies on Ultra-Micro Quantities of Organometallic Compounds. I. On the Determination of the Composition of an Organometallic Compound in an Ultra-Micro Amount

By Tomitaro ISHIMORI

(Received November 11, 1953)

The composition of an organometallic complex compound is usually determined by the chemical analysis of the pure crystals of the complex compound. For the determination of the composition of a complex compound in a minute amount, some optical or electrochemical methods are available, but these methods are not applicable for a complex salt in an ultra-micro amount. However, there are many complex compounds which can be prepared only in extremely minute quantities, e.g. organometallic compounds of much rarer elements such as polonium, promethium and so on.

Recently the present author[1] reported the formation of polonium dithizonate by the dithizone extraction method. The dithizonate has been used in the determination of radium A and radium F in waters of some strongly radioactive hot springs. Also in Europe, G. Bouissieres et al.[2] purified polonium by means of the extraction of polonium dithizonate. Further, radium B content of waters of hot springs was determined by the extraction in the form of lead (radium B) dithizonate.[3]

Such being the circumstances, the author attempted to determine the composition of organometallic compounds which are difficult to prepare in a large amount and devised a method suitable for this purpose. In the present paper, the theoretical basis of the method and the results of the experiments with lead (thorium B) dithizonate and lead (thorium B) hydroxyquinolate, both of the well known compositions, are described.

(A) Theoretical Basis of the Method.

In 1941, I. M. Kolthoff and E. B. Sandell[4] studied the extraction of zinc dithizonate quantitatively and gave an equation relating the extraction coefficient of the metallic dithizonate, the *p*H of the aqueous solution being extracted and the concentration of the chloroform solution of dithizone used for the extraction.

Recently the principles of solvent extraction were outlined by M. Calvin.[5] Basing his results on his theory, Furman determined

1) T. Ishimori and H. Sakaguchi, *J. Chem. Soc. Japan*, **71**, 327 (1950).

2) G. Bouissieres and C. Ferrandini, *Anal. Chem. Acta*, **4**, 610 (1950).

3) H. Umemoto, *Japan Analyst*, **2**, 201 (1953).

4) I. M. Kolthoff and E. B. Sandell, *J. Am. Chem. Soc.*, **63**, 1906 (1941).

5) M. Calvin, *Experientia*, **6**, 135 (1950); *Manhattan Project Report* CN-2486, December 19, 1944; cf. A. E. Martell and M. Calvin, "Chemistry of the Metal Chelate Compunds", N. Y., Prentice Hall Inc., 1952, p. 451.

the chemical formulea of various dithizonates.[6] Moreover, also in Sweden, comprehensive studies on thorium acetylacetonate seem to be carried out from the theoretical points of view.[7]

In a similar way the present author studied the equilibrium between the aqueous solution of a definite *p*H containing a tracer amount of radioisotope of a metallic element and the chloroform solution of an organic reagent, both being in mutual contact.

In such a system the following equilibria are established after thorough shaking and standing:

(organic solvent phase) (aqueous phase)

$$HR \overset{p_r}{\rightleftharpoons} HR \overset{k_r}{\rightleftharpoons} H^+ + R^-$$

Here, an organic reagent, HR, is considered as a weak acid and k_r and p_r respectively indicate the dissociation constant and the partition coefficient as given by Eq. 1 and 2:

$$k_r = [H^+]_w \cdot [R^-]_w / [HR]_w \quad (1)$$

$$p_r = [HR]_w / [HR]_o \quad (2)$$

Here the suffixes, r, w, and o respectively represent the organic reagent, aqueous phase, and organic solvent phase, and the square bracket represents concentration.

Further, the reaction of the metal ion, M^{n+}, with the organic anion and the partition of the organometallic compound, MR_n, between two liquid phases are written as

organic solvent phase) (aqueous phase)

$$MR_n \overset{p_c}{\rightleftharpoons} MR_n \overset{k_c}{\rightleftharpoons} M^{n+} + nR^-$$

Therefore, the equilibrium constant for this reaction is

$$k_c = [M^{n+}]_w \cdot [R^-]^n_w / [MR_n]_w, \quad (3)$$

and the partition coefficient of the complex compound between the aqueous and organic phases is

$$p_c = [MR_n]_w / [MR_n]_o. \quad (4)$$

In these equations, the suffix c represents the complex compound.

The extractability, E, namely the ratio of the radioactivity due to the total amount of the radioactive metallic cation taken into the system and that extracted into the organic phase, is written as

$$E = [MR_n]_o \cdot v_o / ([MR_n]_o \cdot v_o + [MR_n]_w \cdot v_w + [M^{n+}]_w \cdot v_w), \quad (5)$$

where v_o and v_w represent respectively the volumes of the organic and aqueous phases. Introducing values from Eqs. 2, 3 and 4, Eq. 5 beomes

$$E = p_c^{-1} \cdot [MR_n]_w \cdot v_o / [MR_n]_w \cdot \{(p_c^{-1} v_o + v_w) + k_c v_w [R^-]_w^{-n}\}. \quad (6)$$

Because p_c and k_c are constant at a definite temperature and v_o and v_w can be kept constant in a series of experiments, Eq. 6 is simplified as

$$E = 1/(A + B'[R^-]_w^{-n}) \quad (7)$$

or

$$E^{-1} = A + B'[R^-]_w^{-n}, \quad (8)$$

where A and B' are constants.

In Eq. 7 or 8, $[R^-]_w$ is difficult to determine experimentally, but in these cases we consider, $[R^-]_w$ is proved to be proportional to the amount of the organic reagent, (HR), taken into the system. Namely in the equation

$$(HR) = [HR]_o v_o + n[MR_n]_o v_o + [HR]_w v_w + n[MR_n]_w v_w + [R^-]_w v_w, \quad (9)$$

the total amount of metal is so small that second and fourth terms on the right hand side can be neglected. Therefore, Eq. 9 becomes

$$(HR) = [HR]_o v_o + [HR]_w v_w + [R^-]_w v_w. \quad (10)$$

Introducing values from Eq. 1 and 2, Eq. 10 is rewritten as

$$(HR) = [R^-]_w \{k_r^{-1}(p_r^{-1} v_o + v_w)[R^+]_w + v_w\}, \quad (11)$$

where all quantities in the right hand side except $[R^-]_w$ are kept constant. Thus $[R^-]_w$ is proved to be proportional to (HR), and Eq. 8 is rewritten as

$$E^{-1} = A + B(HR)^{-n}, \quad (12)$$

in which A and B are constants.

According to Eq. 12, we can determine the value of n, the ratio between the number of organic anions and that of metallic cation, in the following manner.

An aqueous solution of a definite hydrogen ion concentration containing a known amount of the radioactive tracer of a metal is prepared. In a small separating funnel known volumes of this aqueous solution and an organic solvent containing a known quantity of an organic reagent are shaken together until the equilibrium is established. The organic solvent is then separated and dried in a glass dish. The radioactivity of the residue is measured and the extractability, E is calculated.

Similar procedures are repeated for a series of varying amounts of the organic reagent. The values of E^{-1} are plotted against $(HR)^{-n}$, taking for n the values 1, 2, 3 and so on, so that we can find out the integer, n, which gives the best linearity between E^{-1} and $(HR)^{-n}$.

Thus we can determine the actual value of n, but this method does not give any

6) cf. Martel and Calvin, ibid p. 453. The present author can not find where this paper appeared originally.

7) J. Rydberg, *Arkiv für Kimi*, 5, 517 (1953). This is the eleventh report of Rydberg's study. The rest of this series have not been accesible to the present author.

knowledge concerning the water bound to the complex molecule. Moreover it can not be adopted in the case where two or more kinds of organometallic compounds are formed, and also in the case where the formation of radiocolloids prevents the establishment of the equilibria underlying the derivation of Eq. 12.

In addition to these defects, we can not estimate the effects of impurities introduced into the system by chemicals used in the experiment. Any way the amount of these impurities is supposed to be much greater than the radiochemical amount of the metallic cation taken into the system.

(B) Experimental Examination of the Validity of the method.

As mentioned above, there are many uncertain facts which may disturb the results of the method. Therefore, the author intended to check the validity of the above reasoning for some organometallic compounds such as lead dithizonate and lead hydroxyquinolate, the composition of which are known already. In these experiments carrier-free radioisotope of lead, thorium B, is used.

(1) Preparation of thorium B solution.

According to the usual method recommended by O. Hahn[8], the radioactive deposits of thoron are collected on a platinum plate. About 50 g. thorium nitrate is placed in a closed metal container into which an insulated, negatively charged (250 volts) platinum plate is also introduced. The active deposit proceeding from the emanation, i. e. thorium B with its disintegration products, is collected on the platinum plate for about 24 hours, and then dissolved into hot dilute nitric acid (1 : 15). The solution is made up to 25cc. and divided into aliquot portions for both the preparation of the standard specimen of thorium B and the following experiments.

The radiochemical purity is examined by the measurement of the decay curve shown in Fig. 1, in which the logarithm of the activity is plotted against the time elapsed. From this figure the apparent half-life of the activity is calculated as about 10.5 hours. So we can conclude that the "thorium B" will not have any detectable radiochemical impurity except its daughter, thorium C group, in an equilibrium amount.

The measurements of the activities are carried out by a Lauritsen electroscope made by the Scientific Research Institute, Tokyo.

Owing to its relatively short half-life (10.6 hours), the solution of thorium B must be prepared just before each series of experiments so that its radioactivity is measured accurately.

(2) On the composition of lead dithizonate.

5cc. of 50% sodium citrate solution and and 5cc. of 10% potassium cyanide are added to 20cc. of thorium B solution obtained as above. Ammonium hydroxide is added to the mixture dropwise to make it weakly alkaline, and the resultant solution is made up to 100cc. The pH of the solution is checked by a pH test paper and estimated to be about 9.5.

The stock chloroform solution of dithizone (about 1.25×10^{-4} mol./1.)[9] is diluted successively with chloroform and a series of chloroform solutions of dithizone, 1, 1/5, 1/10, 1/25 and 1/50 times the concentration of the original stock solution, is prepared. Dilution of the solutions is made just before use to prevent the decomposition of dithizone.

To 10 cc. of the aqueous solution prepared as above, 5 cc. of the chloroform solution of dithizone (known concentration) are added in a separating funnel. The system of the two liquid phases is shaken vigorously for one minute and is left to stand aside for a while so that it separates into two liquid phases. The chloroform phase is taken into a glass dish, dried up and left to stand overnight before the measurement of radioactivity. During the overnight standing, thorium B disintegrates to a considerable extent, so it looks unfavorable for the measurement of radioactivity, but it is necessary to make sure the condition of radiochemical equilibrium between thorium B and its daughters, members of thorium C group.

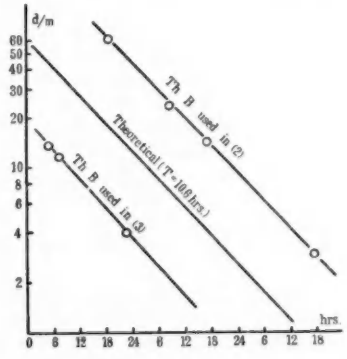


Fig. 1

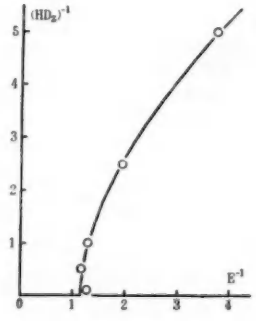


Fig. 2 a

8) Otto Hahn, "Applied Radiochemistry" Cornell Univ. Press, New York, N. Y., p. 44 (1936).

9) The concentration of dithizone in chloroform is determined by titrating a dilute solution of silver nitrate.

Taking the ratio of the activity due to the extracted thorium B to that of the standard specimen of the same age, the extractability, E, is calculated.

Similar procedures are repeated for varying concentrations of dithizone in chloroform.

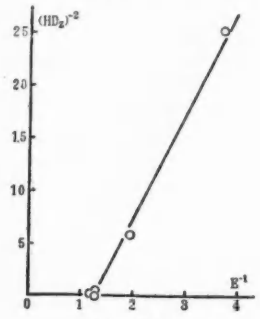


Fig. 2 b

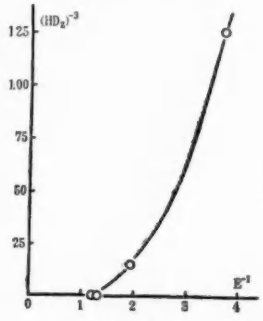


Fig. 2 c

TABLE I

RESULTS FOR LEAD DITHIZONATE

No.	(HDz)	$(HDz)^{-1}$	$(HDz)^{-2}$	$(HDz)^{-3}$	E^{-1}
1	10	0.1	0.01	0.001	1.27
2	2	0.5	0.25	0.125	1.19
3	1	1.0	1.0	1.0	1.30
4	0.4	2.5	6.3	15.6	1.97
5	0.2	5.0	25.	125.	3.72

(HDz): Amount of dithizone in an arbitrary unit in which about $6.3\ 10^{-7}$ mol. dithizone corresponds to (HDz)=10

E : Extractability

Results obtained are shown in Table I and Fig. 2 (a, b, c). As can be seen in these figures, E^{-1} is linear to $(HDz)^{-2}$. (cf. Fig. 2 b) So we can conclude that the composition of lead dithizonate is of such a ratio as when one atom of lead is bound to two anions of dithizone, Dz.

On the other hand Liebhasky and Winslow[10] reported that lead dithizonate corresponds to the formula $PbDz$, but Clifford[11] showed that the complex compound is actually $PbDz_2$, which is generally accepted by most chemists.[12] The conclusion obtained by the present method also coincides with that of Clifford. Therefore, the present method is considered to be applicable for the determination of the composition of organometallic compounds. And the disturbing factors mentioned above proved to result in no serious error.

(3) On the composition of lead hydroxyquinolate.

To the solution which contains 5g. sodium citrate and 20 cc. thorium B solution described in (1), ammonium hydroxide is added dropwise until *p*H of the solution becomes about 9. The resultant solution is made up to 50 cc.

About 100 mg. 8-hydroxyquinoline is dissolved in 50 cc. chloroform. Diluting this solution with chloroform, a series of solutions of 8-hydroxyquinoline is prepared. Their concentrations are 1, 2/5, 1.5/5, and 1.2/5 times that of the original solution.

Using the aqueous solution of thorium B and the chloroform solution of 8-hydroxyquinoline, a series of experiments is carried out in a similar way as described in the case of lead dithizonate.

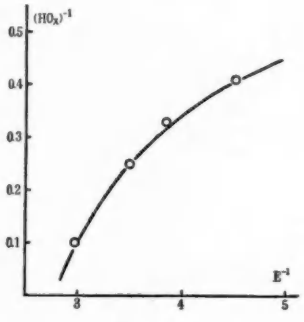


Fig. 3 a

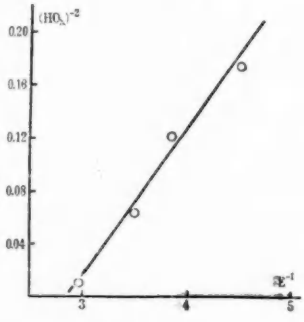


Fig. 3 b

10) H. A. Liebhasky and E. H. Winslow, *J. Am. Chem. Soc.* **59**, 1966 (1937).

11) P. A. Clifford, *J. Official Agr. Chem.* **26**, (1943); *C. A.*, **37**, 3009.

12) The formula given by Clifford which coincides with that of H. Fischer (*Z. anorg. Chem.*, **47**, 685 (1934).) is quoted by F. J. Welcher ("Organic Analytical Reagents", vol. 3, D. van Nostrand Co., Inc., New York, 1947. p. 470.).

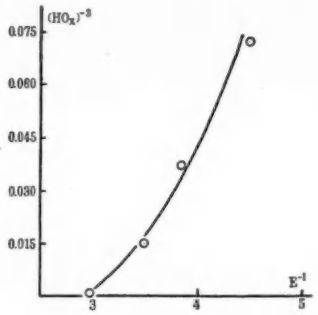


Fig. 3 c

TABLE II.

RESULTS FOR LEAD HYDROXYQUINOLATE

No.	(HOx)	$(HOx)^{-1}$	$(HOx)^{-2}$	$(HOx)^{-3}$	E^{-1}
1	10	0.1	0.01	0.001	2.97
2	4	0.25	0.063	0.015	3.50
3	3	0.33	0.111	0.037	3.84
4	2.4	0.41	0.174	0.072	4.51

(HOx): Amount of 8-hydroxyquinoline in an arbitrary unit in which (HOx) = 10 corresponds to about 10 mg. 8-hydroxyquinoline.

E : Extractability

The results are shown in Table II and in Fig. 3 (a, b, c). In Fig. 3 b, we can see a linear relationship between E^{-1} and $(HOx)^{-2}$. Therefore we can conclude that lead hydroxyquinolate corresponds to the formula $Pb(Ox)_2$. This conclusion agrees with the generally accepted formula[13] for lead hydroxyquinolate, again showing the applicability of the present method method for such a problem.

In the following papers results for some organometallic compounds which have unknown compositions will be reported.

The author has to thank to Professor Tsunetaka Sasaki, Kyushu University, for his encouragement and criticism in several discussions on the theoretical considerations of the present study.

Department of Chemistry, Faculty of Science, Kyushu University, Fukuoka

13) V. Maarson and L. W. Haase, *Chem. Ztg.* **52**, 993 (1928); *C. A.* **23**, 1077 (1928).

On the Ring-opening Reactions of the Furan Compounds. IV. The Condensation Products of Furfural with Methyl Propyl Ketone, Methyl Isopropyl Ketone and Pinacolin by Alkali

By Hiroshi MIDORIKAWA

(Received November 17, 1953)

In the previous paper[1] it was reported that, in the condensation of furfural and benzaldehyde with methyl ethyl ketone by alkali, the lowered reaction temperature (0~5°) favored the aldol condensation at the α-methylene group of the ketone and the elevated reaction temperature (60~65°) the condensation at the α-methyl group of the ketone. In the present work were studied the condensation of furfural with methyl propyl ketone by alkali and the ring-opening of the condensation products of furfural with methyl isopropyl ketone and pinacolin.

The condensation of furfural with methyl propyl ketone was carried out in two cases of lowered and elevated reaction temperatures, 0~5° and 60~63°.

In both cases, the condensation products afforded two species of semicarbazone—a greater amount of colorless needle crystals melting at 143~144° and a much smaller amount of colorless needles melting at 223~225°. The ratios of the semicarbazone melting at 143~144° to that melting at 223~225° in the two cases were nearly equal. Considered from the analysis, the condensation product at the lowered reaction temperature appeared to contain a small quantity of the aldol condensation product which corresponds to that of furfural with methyl ethyl ketone.

The condensation product at the reaction temperature 0~5°, after heating with dilute hydrochloric acid in order to dehydrate the aldol[2] which was considered to be contained, was oxidized by sodium hypochlorite to give α-ethyl-2-furanacrylic acid (IV), in the fol-

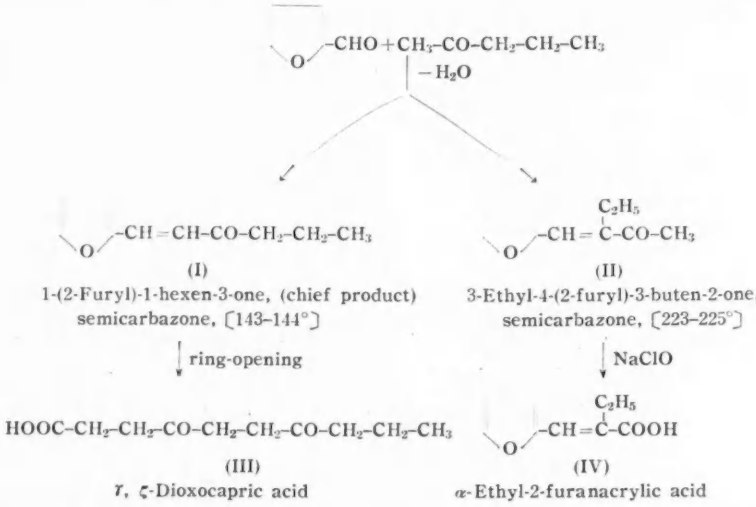
1) H. Midorikawa: This Bulletin, **26**, 460 (1953).

2) H. Midorikawa: This Bulletin, **26**, 462 (1953).

lowing formulation, although in a very poor yield. Consequently it is evident that 3-ethyl-4-(2-furyl)-3-buten-2-one (II) is contained in it and methyl propyl ketone reacts with furfural at the α-methylene group of the ketone. The condensation product at the reaction temperature 0~5°, after being heated with dilute hydrochloric acid, gave a mixture of a larger proportion of the semicarbazone melting at 143~144° and a much smaller proportion of that melting at 223~225°.

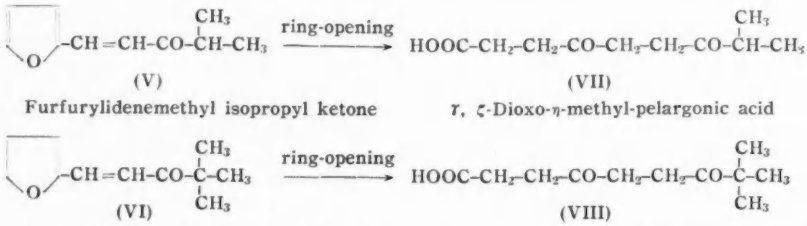
The condensation product at the reaction temperature 60~63°, on the ring-opening in alcoholic hydrochloric acid[3], gave a dioxocarboxylic acid in a good yield. This acid was considered to be identical with the dioxocarboxylic acid which was reported as γ, ζ-dioxocapric acid (III) by Breusch and Ulusoy[4].

From the stand-point of the poor yield of α-ethyl-2-furanacrylic acid (IV) and the good yield of γ, ζ-dioxocapric acid (III), it was infered that 3-ethyl-4-(2-furyl)-3-buten-2-one(II), which furnished the former acid on the treatment with sodium hypochlorite, gave the semicarbazone of colourless needles (m. p. 223~225°), and the furfurylidene ketone which gave the semicarbazone of colorless minute needles (m. p. 143~144°) was 1-(2-furyl)-1-hexen-3-one (I) yielding γ, ζ-dioxocapric acid (III) by the ring-opening, as shown below.



The poor yield of α-ethyl-2-furanacrylic acid (IV) appeared to reveal a weaker reactivity of the α-methylene group of methyl propyl ketone in comparison with that of methyl ethyl ketone.

The condensation products of furfural with methyl isopropyl ketone and pinacolin by alkali, furfurylidenemethyl isopropyl ketone (V) and furfurylidene-methyl tert-butyl ketone (VI), gave γ, ζ-dioxo-η-methylpelargonic acid (VII) and γ, ζ-dioxo-η, η-dimethylpelargonic acid (VIII) respectively, on the ring-opening in alcoholic hydrochloric acid. These reactions are illustrated as follows:



3) E. A. Kehrer and P. Igler: *Ber.*, **32**, 1177 (1899).
4) F. L. Breusch and E. Ulusoy: *C. A.*, **42**, 5850 (1948).
5) I. Kashiwagi: This Bulletin, **1**, 94 (1926).

Experimental

Condensation of Furfural with Methyl Propyl Ketone Into a stirred suspension of methyl propyl ketone (13 g.) and furfural (7 g.) in water (150 cc.) was at once introduced 5 % aqueous sodium hydroxide (10 cc.) at 60~63°. The reaction was complete after stirring for 2.5 hrs. at 60~63°. The reaction mixture was neutralised with dilute sulfuric acid. The oily layer was separated and the aqueous solution extracted twice with ether. The combined ethereal solution of the oily layer and the ether extract, after drying over anhydrous sodium sulfate, was fractionated to give a yellow liquid (7 g.), b. p. 119~121°/8 mm.

This fraction was considered to consist of 1-(2-furyl)-1-hexen-3-one (I) in a larger proportion and 3-ethyl-4-(2-furyl)-3-buten-2-one (II) in a much smaller proportion.

Calcd. for $C_{10}H_{12}O_2$: C, 73.12, H, 7.37 %; Found: C, 72.92, H, 7.60 %.

This oil gave a mixture of two species of semicarbazone. The greater part consisted of colorless microscopic needles, which were fairly soluble in methanol and melted at 143~144° on recrystallisation from methanol-water. In addition, fewer colorless needles, which were sparingly soluble in cold methanol and recrystallised from methanol, m.p. 223~225°, were obtained.

The semicarbazone melting at 143~144° was considered to be that of 1-(2-furyl)-1-hexen-3-one (I).

Calcd. for $C_{11}H_{15}O_2N_3$: C, 59.69, H, 6.83, N, 18.99 %; Found: C, 59.55, H, 6.86, N, 19.12 %.

In a solution of 2, 4-dinitrophenylhydrazine in methanolic sulfuric acid, this semicarbazone was converted to a 2, 4-dinitrophenylhydrazone, which was recrystallised from pyridine in red foliated crystals, m. p. 171~172°.

Calcd. for $C_{16}H_{16}O_5N_4$: C, 55.79, H, 4.68, N, 16.27 %; Found; C, 55.74, H, 4.43, N, 16.57 %.

The semicarbazone melting at 223~225° was considered to be the one of 3-ethyl-4-(2-furyl)-3-buten-2-one (II).

Calcd. for $C_{11}H_{15}O_2N_3$: C, 59.69, H, 6.83, N, 18.99 %; Found: C, 59.69, H, 6.89, N, 18.79 %.

This semicarbazone was also converted to 2, 4-dinitrophenylhydrazone which was recrystallised from pyridine in carmine prisms, m. p. 183~184°.

Calcd. for $C_{16}H_{16}O_5N_4$: C, 55.79, H, 4.68, N, 16.27 %; Found: C, 55.81, H, 4.45, N, 16,21 %.

The condensation at 0~5° also was carried out by stirring a mixture of methyl propyl ketone (15 g.), furfural (8 g.), water (150 cc.) and 10 % aqueous sodium hydroxide (10 cc.) for 7 hrs. The reaction mixture was kept overnight below 10°, and then worked up in the same manner as in the condensation at 60~63°. A fraction (7.5 g.) distilling at 119~123°/8 mm was collected.

Calcd. for $C_{10}H_{12}O_2$: C, 73.12, H, 7.37 %; Found: C, 70.34, H, 7.62 %. (This analysis seems to show that this fraction contains a small amount of the aldol condensation product, $C_4H_3O{\cdot}CH(OH)CH(CH_3){\cdot}CO{-}CH_3$, which requires C, 65.89 %; H, 7.74 %.)

This fraction gave the same semicarbazones as the condensation product at the reaction temperature 60~63°.

Ring-opening of the Condensation Product of Furfural with Methyl Propyl Ketone The condensation product (2 g.) at the reaction temperature 60—63° was refluxed with conc. hydrochloric acid (1.5 cc.) and alcohol (5 cc.) for 3 hrs. The reaction mixture was evaporated till dry in the water-bath, and a small quantity of dil. hydrochloric acid was added to evaporate till dry once more. The residue was extracted with a sufficient quantity of water, and the extract was concentrated on the water-bath to give the dioxocarboxylic acid which was considered to be γ, ζ-dioxocapric acid (III) (0.7 g.). The acid was recrystallised from ligroin as colorless hexagonal plates, m.p. 83~84°; lit.,[4] m.p. 83~84°.

Calcd. for $C_{10}H_{16}O_4$: C, 59.96, H, 8.00 %; Found: C, 60.40, H, 8.14 %.

Sodium Hypochlorite Oxidation of the Condensation Product of Furfural with Methyl Propyl Ketone The condensation product(2.3g.) at the reaction temperature 0~5° was suspended in 6 % hydrochloric acid (5 cc.) and heated by shaking in the water-bath for a short time. The separated oil was suspended in the aqueous sodium hypochlorite solution[2] (15 cc.) and kept at ordinary temperature for two days, with occasional shaking. The reaction mixture was freed of the oily matter by extraction with ether and acidified with dilute hydrochloric acid to yield a small number of crystals, which were dissolved in a requisite quantity of hot water, decolorised with active charcoal and crystallised as colorless needles on cooling, m.p. 95~96°. This specimen showed no depression on admixture with α-ethyl-2-furanacrylic acid which was synthesised by the reaction of furfural with butyric anhydride and anhydrous sodium butyrate.[5]

Ring-openings of Furfurylidenemethyl Isopropyl Ketone (V) and Furfurylidenemethyl *tert*-Butyl Ketone (VI) Furfurylidenemethyl isopropyl ketone (V) and furfurylidenemethyl *tert*-butyl ketone (VI) were respectively synthesised by the condensations of furfural with methyl isopropyl ketone and pinacolin, using sodium hydroxide as the condensing agent.[5]

Furfurylidenemethyl isopropyl ketone (b.p. 101~102°/5 mm.) gave a semicarbazone crystallising from methanol-water as colorless needles, m.p. 148~149°, and a 2, 4-dinitrophenylhydrazone crystallising from pyridine as orange needles, m.p. 175~176°.

Semicarbazone. Calcd. for $C_{11}H_{15}O_2N_3$: C, 59.69, H, 6.83, N, 18.99 %; Found: C,59.98, H, 6.89, N, 18.97 %. *2, 4-Dinitrophenylhydrazone* Calcd. for $C_{16}H_{16}O_5N_4$: C, 55.79, H, 4.68, N, 16.27 %; Found: C, 55.57, H, 4.33, N, 16.30 %.

Furfurylidenemethyl *tert*-butyl ketone (b.p. 101~102°/5 mm.) gave no semicarbazone, as reported by Kashiwagi,[5] but gave a 2, 4-dinitrophenylhydrazone crystallising from pyridine-methanol as scarlet lustrous needles, m.p. 121~123°.

6) A. S. Carter: *J. Am. Chem. Soc.*, 50, 2299 (1928).

Calcd. for $C_{17}H_{18}O_5N_4$: C, 56.98, H, 5.07, N, 15.63 %; Found: C, 57.03, H, 5.03, N, 15.62 %.

The ring-opening of furfurylidenemethyl isopropyl ketone (2 g.) was carried out by refluxing with conc. hydrochloric acid (1.5 cc.) and alcohol (5 cc.) for 3 hrs. By the same procedure as in the case of the foregoing ring-opening reaction was obtained τ, ζ-dioxo-η-methylpelargonic acid, which was recrystallised from ligroin as colorless needles, m.p. 72~73°.

Calcd. for $C_{10}H_{18}O_4$: C, 59.96, H, 8.00 %; Found: C, 59.93, H, 7.89 %.

The ring-opening reaction of furfurylidenemethyl *tert*-butyl ketone to τ, ζ-dioxo-η, η-dimethylpelargonic acid (VIII) was performed by the same procedure as in the case of furfurylidenemethyl isopropyl ketone. The ketone (2 g.) gave the crude acid (0.5 g.) as a viscous oil. It was recrystallised from ligroin as colorless leaflets, m.p. 46~47°.

Calcd. for $C_{11}H_{18}O_4$: C, 61.64, H, 8.47 %; Found: C, 61.57, H, 8.39 %.

Summary

Methyl propyl ketone condensed with furfural by alkali both at the α-methyl and α-methylene groups of the ketone, giving 1-(2-furyl)-1-hexen-3-one (I) in a larger proportion and 3-ethyl-4-(2-furyl)-3-buten-2-one (II) in a much smaller proportion.

The former furfurylidene ketone (I) gave τ, ζ-dioxocapric acid (III) on the ring-opening in alcoholic hydrochloric acid, and the latter (II) was oxidized by sodium hypochlorite to α-ethyl-2-furanacrylic acid (IV).

The ring-opening of furfurylidenemethyl isopropyl ketone (V) and furfurylidenemethyl *tert*-butyl ketone (VI) in alcoholic hydrochloric acid gave τ, ζ-dioxo-η-methylpelargonic acid (VII) and τ, ζ-dioxo-η, η-dimethylpelargonic acid (VIII) respectively.

The author expresses his sincere thanks to Dr. T. Hayashi for his kind advice.

Scientific Research Institute,
Komagome, Bunkyo-ku,
Tokyo

The Structure of Surface Denatured Protein. VI. The Effect of pH of Substrate upon the Limiting Area of Protein Monolayer

By Kazutomo IMAHORI

(Received November 26, 1953)

Introduction

Gorter[1] has investigated the influence of *p*H of the substrate upon the spreading of various proteins, by measuring the spreading areas after the protein has been in contact with solutions of different *p*H for a period of one or two minutes. He observed that such protein as egg albumin or serum albumin, spread well at the *p*H of its isoelectric point, as well as in the case of strong alkaline and strong acid solutions, but on both sides of the isoelectric point, little spreading could be obtained. But the low spreading disappeared, when enough salt was added to the substrate. These results can be explained[2] by assuming that at *p*H values, where the effective protein charge is high, the spreading tendency is at a minimum. Yet, the truth of the above assumption has not been ascertained. The author has studied the size and the shape of protein molecules expanded on substrates of various *p*H values, and has considered the cause of spreading from these results.

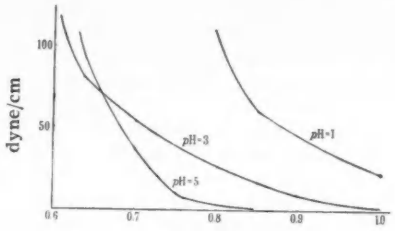
1) E. Gorter, H. Ormondt, and F. Dom, *Proc. Kon. Akad. v. Wet.*, **35**, 838 (1933).
2) E. Gorter 'Surface tension and films' Schmit's Chem. of the amino acids and proteins. p. 428.

The Limiting Area

The limiting areas of the surface films of egg albumin as well as horse serum albumin have been measured. Both samples are in the pure crystalline state, being prepared by Drs. S. Nakamura and H. Sugano at the Chem. Inst. of Tokyo University. The apparatuses used for this measurement are a surface balance and than ellipsometer, the former of which has been described in the first report of this series[3], while the details of the latter will be published shortly. Three buffer solutions having the *p*H values of 1, 3, (HCl buffer) and 5 (acetate buffer), are used as the substrates.

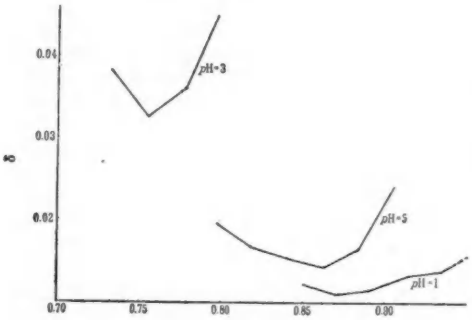
The F—A relations of serum albumin films on these three buffers are shown in Fig. 1. These would suggest many things. First of all, the curve on *p*H=5 is of a condensed type, while the other two are of an expanded type. The curve of *p*H=1 breaks at the area of 0.845 m^2/mg, and the curve of *p*H=5, at 0.76 m^2/mg, but the curve of *p*H=3, at the area of 0.637 m^2/mg.

Similar features can be seen in the case of egg albumin. In Fig. 2, π—A relations of egg albumin



m^2/mgs

Fig. 1.



m^2/mg

Fig. 2

are shown instead of those of F—A, where δ means the compressibility, being defined by the following relation:

$$\delta = -\frac{1}{A} \cdot \frac{dA}{dF}$$

The δ—A relations on pH=1 and pH=5 are similar, and the minima of both curves are at 0.87 and 0.86 m^2/mg respectively. But the curve of pH=3 has a far smaller limiting area (0.755 m^2/mg). Fig. 2 shows also that the δ min (the value of δ at the minimum point) on pH=3 is greater than those on pH=1 and pH=5. This means of course, that the film of egg albumin which expanded on the substrate of pH=3 is more compressible than those on pH=1 and pH=5. This fact seems to have some relation to the results of the following experiment.

The films which expanded on the substrates of various pH values were transferred on the metallic slide, by Blodgett's method, under the surface pressure of 13 dynes/cm, and 30 dynes/cm.

The thicknesses of these films were measured by using the ellipsometer. The results were as follows. The films expanded on pH=1 and pH=5 showed the same and constant thickness,—about 10 Å—if they were built up under the pressure of 13 dynes/cm or 30 dynes/cm. But the film on pH=3 had as well the thickness of 10 Å when it was built up under the pressure of 13 dynes/cm., but its thickness increased to 25 Å, when it was built up under the pressure of 30 dynes/cm. This result would suggest that the egg albumin molecules, which were denatured and expanded on the solution of pH=3, might be easily again folded into thicker ones, being in accordance with the fact of the large δ value of this film.

The Size and the Shape

The molecular weight of egg albumin which expanded on the solutions of pH=1 and pH=3, has been determined by the method of Bull and Guastalla[4]. The molecular weight thus obtained was about 42,000 in both cases. This value is just between those obtained by Bull and Guastalla. On the other hand, the molecular weight of serum albumin has been obtained as 70,000 in the previous paper[3].

From these values and the limiting areas obtained above, we can calculate the surface area of each protein molecule as shown on the third line of Table I.

The shape of a protein on each substrate might be determined by the experiment of surface diffusion. The details of the experiment and also of the way of calculation, were given in the second and third reports of this series[5,6].

TABLE I

	Egg albumin			Serum albumin		
pH	1	3	5	1	3	5
surface area per molecule	6065 Å²	5260 Å²	60000 Å²	9830 Å²	7380 Å²	8840 Å²
axial ratio	30:1	15:1		20:1	10:1	8:1
short axis	28.5 Å	37.5 Å		44.4 Å	54.5 Å	66.7 Å
long axis	855 Å	562 Å		888 Å	545 Å	533 Å

The results are also shown on the fourth line of Table I. The shape, being assumed to be an elliptic disk, is expressed in terms of the axial ratio. On the fifth line of the table, the lengths of two axes are given.

The data in Table I suggest that the shape of the snrface-denatured protein molecule of both albumin species depends on the pH value of the substrate. The molecules expanded on the acid substrate have extremely elongated shapes. This conclusion ascertained by experiment of surface viscosity. Fig. 3 shows the results of the mea-

3) K. Imahori, This Bulletin, **27**, 7 (1952).
4) H. B. Bull, "Advances in Protein Chemistry." Vol. 3.
5) K. Imahori, This Bulletin **27**, 9, (1952).
6) K. Imahori, This Bulletin **27**, 11 (1952).

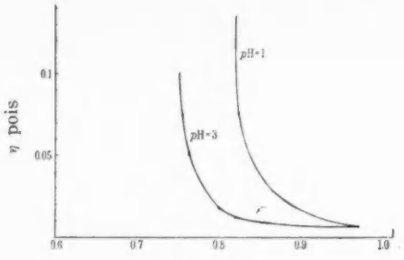


Fig. 3

surements of surface viscosity against the surface area, indicating that the film of egg albumin expanded on pH=1 solution has far greater viscosity than that on pH=3. Similar results are obtained, if we measure the surface viscosity of the serum albumin on pH=1 and pH=5. The high viscosity of both albumins on pH=1, shows that these protein molecules have elongated shapes on the acid substrate.

Discussions

The results of the preceding experiments show that each molecule of two albumin species takes a different form in the three different solutions. The molecule expanded on the solution of pH=1, has the most elongated shape. It forms well expanded, quite thin, and the least compressible rigid films.

The molecule expanded on pH=3, shows a less elongated shape. As it is more compressible than that on pH=1, it is presumably folded into the thicker film under high surface pressure.

The molecule on pH=5, shows also a less elongated shape as in the case of pH=3. But it makes a well-expanded, incompressible rigid film.

The F—A curve of this latter film is of the condensed type, indicating that interaction between molecules is fairly small.

These differences may be explained to some extent as follows. On the solution of pH=1, the basic residues of the albumin molecule, such as arginine, or lysine are ionized and carry the positive charge, while the acid residues such as glutamic acid or asparatic acid are not ionized in this pH range and consequently carry no charge.

The positive charges of those basic residues act repulsively on each other. On the other hand, they are very hydrophilic and are apt to put themselves into the water. The former causes the albumin molecules to be perfectly unfolded, and to take an extremely elongated shape. The latter causes them to lie flat on the water surface, and to make a stable rigid film. Each molecule carries a number of net positive charges, which cause the molecules to repulse each other, and makes the F—A curve into an expanded one.

On the substrate of pH=5, on the other hand, most of the acid and basic residues are ionized, and the albumin molecule contains about an equal number of negative and positive charges upon it. These charges of different signs, acting attraction force on each other and leading to inter- and intramolecular salt-like bonds, as well as hydrogen bonds, and S-S bonds, will prevent the albumin molecule from being perfectly unfolded. Thus, the albumin molecule on pH=5, containing bended structure, takes rather a round shape. The intra-molecular bonds also make the polypeptide chain assume a definite structure, which leads to the comparatively large limiting area and low compressibility as is seen in the above experiment. As the molecule contains many ionized and hydrophilic residues, it can make the stable, incompressible and rigid film. On the substrates of pH=3, the number of positively charged residues of the albumin molecule is less than that of pH=1, while, some of the acid residues can be ionized in this case. Thus, the intra-molecular repulsive force is not so strong as that of pH=1, while the intramolecular bonds are not enough to hold the rigid and bended structure, on the water surface. Thus, the molecule on pH=3 is very flexible, yields easily to external force and causes the low limiting area. A small number of charges make the film somewhat hydrophobic and compressible into a thicker film, under high surface pressures.

This contraction and expansion of the film caused by the variation of pH of the substrate was observed with a mixed film of octadecyl amine and stearic acid as well.

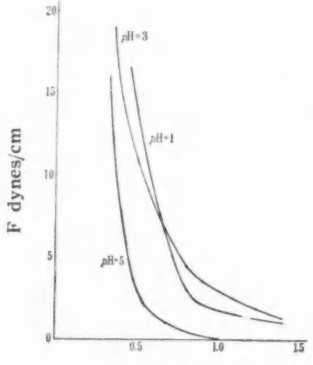


Fig. 4

The details of the experiment will be published elsewhere in the near future.

The following experiment supports our explanation. In Fig. 4, the F—A curve of the heat denatured serum albumin is shown. The procedure was nearly the same as that of S. Staelberg[7]. The same crystalline serum albumin was dissolved in 60% n-propyl alcohol containing 0.5 M sodium acetate, and denatured by heating at 100°C for 30 minutes. The protein spread from this solution gave the limiting areas of 0.82 and 0.55 m²./mg. on the substrates of pH=1 pH=5 respectively. The F—A curve of the film on pH=3 broke slightly at the area of about 0.82 m²./mg., but the film might be compressed to the limiting area of 0.55 m²./mg. The small limiting area on pH=5 means that the intra-molecular bonds were broken by heat, and so the molecules were readily compressible by the attraction between residues of different signs. On the substrate of pH=1, however, few differences were found between the heat-denatured and not heat-denatured proteins. The breaking of intra-molecular bonds by heat resulted in a good expansion of protein on the substrate of pH=3. As the repulsive force was not so remarkable as on pH=1, the molecule could be easily compressed into the compact state as on pH=5.

7) Stina Staelberg, *Trans. Faraday Soc.*, **35**, 1416 (1939).

Conclusion

(1) The size and shape of the egg and serum albumins have been measured on three buffer solutions having the pH values of 1, 3, and 5 respectively.

(2) The film on pH=1 is a well-expanded, incompressible and rigid one. That on pH=5 is as well expanded, but the film on pH=3 is of a not well expanded but easily compressible type.

(3) These differences have been discussed from the points of charges and intra-molecular bonds.

The author wishes to express his hearty thanks to Prof. Bun-ichi Tamamushi, for his kind inspection of this paper. Some part of the present work has been aided by Miss Mitsuko Hachiwaka and Miss Harumi Matsui, to whom the author's thanks are due. This experiment is aided by the Scientific Research Encouragement Grant from the Ministry of Education.

Chemical Institute, College of General Education, Tokyo University, Tokyo

The Condensation of Furfural with Methyl Ethyl Ketone by Aqueous Sodium Hydroxide

By Hiroshi MIDORIKAWA

(Received December 7, 1953)

In the previous paper[1], it was reported that, in the condensation of furfural with methyl ethyl ketone by aqueous sodium hydroxide, a mixture of two furfurylidene ketones was obtained and one of those was 4-(2-furyl)-3-methyl-3-buten-2-one (I), and the other was considered to be 1-(2-furyl)-1-penten-3-one (II). In the present experiment, these furfurylidene ketones were completely separated from each other, and the results[1] previously obtained were confirmed.

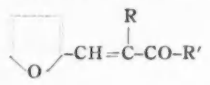
The condensation was carried out at the reaction temperature 60~63°. The resulting condensation product gave a mixture of three species of semicarbazone, foliated crystals (m.p. 212~213°), needle crystals (m.p. 183~184°) and tabular crystls (m.p. 166~167°).

1) H. Midorikawa, This Bulletin, **26**, 460 (1953).

The semicarbazone of foliated crystals (m.p. 212~213°), separating from the other two species by the less solubility in methanol, regenerated a ketone, a pale yellow oil, on heating with dilute hydrochloric acid. This oil afforded α-methyl-2-furanacrylic acid (III) in a good yield on sodium hypochlorite oxidation. Consequently it is evident that this oil is 4-(2-furyl)-3-methyl-3-buten-2-one (I). The reactions are illustrated in the formulation shown below.

By refluxing with alcoholic hydrochloric acid, this ketone did not give γ, ζ-dioxo-ε-methylcaprylic acid, CH_3–CO–CH(–CH_3)–CH_2–CO–CH_2–CH_2–COOH, which was considered to be obtained by the furan ring opening. This result corresponds to the noteworthy fact

that the furfurylidene ketone

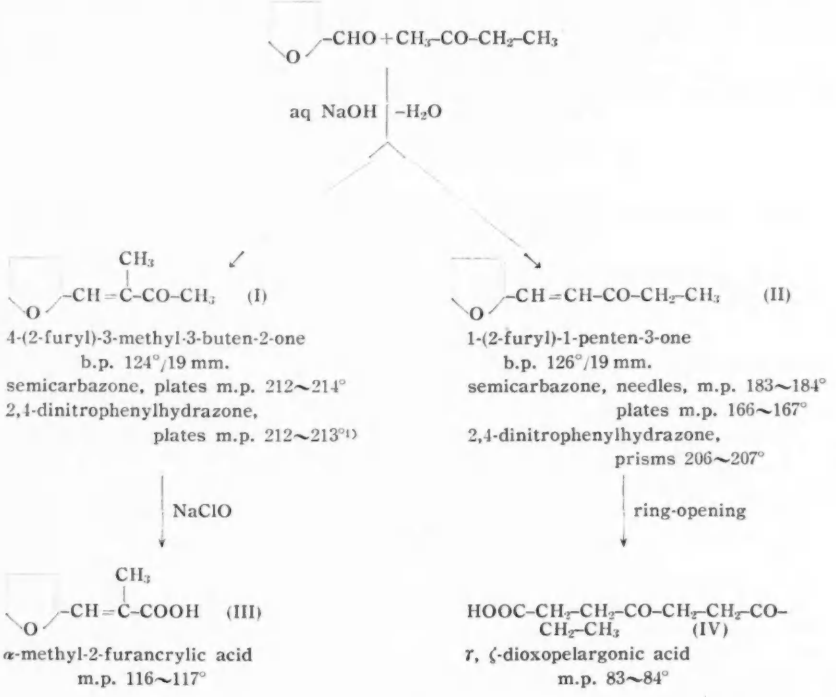


which possesses the alkyl group (R) at the carbon atom joining its carbonyl and furfurylidene groups, as in this keton, does not give the dioxocarboxylic acid R′-CO-CH(R)-CH_2-CO-CH_2-CH_2-COOH by the cleavage of the furan ring when refluxed with alcoholic hydrochloric acid[2], although there are a few exceptions[3].

The semicarbazones of needle crystals (m.p. 183~184°) and tabular crystals (166~167°) which were more soluble in methanol were selected from each other, after several recrystallisations. The latter crystals were not detected in the previous experiment[1]. The needle crystals appeared to shift to the tabular crystals comparatively less soluble in methanol on repeated recrystallisation by methanol-water. These two species of crystals were converted into the identical 2,4-dinitrophenylhydrazone of carmine needles (m.p. 206~207°), when reacted with 2,4-dinitrophenylhydrazine in alcoholic sulfuric acid. Obviously, one species of ketone gave the two species of semicarbazone, although it was not clear whether these two species are two forms in dimorphism or in syn-anti isomerism.

The mixture of these needle and tabular crystals of semicarbazone, on heating with dilute hydrochloric acid, generated a faintly yellow oil. This oil was considered to be 1-(2-furyl)-1-penten-3-one (II), since it generated no heat and gave no chloroform on treatment with aqueous sodium hypochlorite. This ketone gave the dioxocarboxylic acid (m.p. 83~84°) in a good yield, on refluxing with alcoholic hydrochloric acid. It seemed certain that this dioxocarboxylic acid is γ, ζ-dioxopelargonic acid (IV).

The reactions described above are illustrated in the following formulation.



Experimental

Condensation of furfural with methyl ethyl ketone Furfural (60 g.) and methyl ethyl ketone 120 g.) were dissolved in water (1000 cc.), and 10% aqueous sodium hydroxide (50 cc.) was at once run in at 60° with stirring. After prolonged

2) H. Midorikawa: This Bulletin, **26**, 317 (1953).
3) D. L. Turner: *J. Am. Chem. Soc.*, **71**, 612 (1949).

stirring for 1 hr. at 60°, the reaction mixture was worked up in the same manner as in the case of the previous report[1] to give a pale yellow oil (70 g.) distilling at 126~127°/20 mm.

This fraction (30 g.) was suspended in a solution of semicarbazide hydrochloride (30 g.) and sodium acetate (50 g.) in water (40 cc.) and methanol added, until a homogeneous solution was obtained. On standing overnight, crystals (40 g.) of semicarbazone separated out.

The crystals (40 g.) of semicarbazone were heated with methanol (200 cc.) on a water-bath, and, on cooling, a fraction(16 g.) of crystals melting at 205~210° was obtained. This fraction was once more washed with hot methanol (50 cc.) to give colourless crystals (15 g.) melting at 211~213°. From the filtrate pale yellow crystals (25 g.) melting at 130~140° were obtained by addition of a sufficient quantity of water. Several recrystallisations of these crystals from methanol gave a mixture (15 g.) of needles (m.p. 183~184°) previously reported[1] and plates (m.p. 166~167°), which were picked out from each other. On repetition of the recrystallisation, the needle crystals appeared to shift to the tabular crystals less soluble in methanol. Analysis of the tabular crystals (m.p. 166~167°): Found: C, 57.75, H, 6.12, N, 20.16. Calcd. for $C_{10}H_{13}O_2N_3$: C, 57.94, H, 6.32, N, 20.28%.

Both needle and tabular crystals were converted into the 2,4-dinitrophenylhydrazone (m.p. 206~207°), which showed no depression of the mixed melting point with 2,4-dinitrophenylhydrazone (m.p. 205~206°) obtained in the previous experiment[1].

4-(2-Furyl)-3-methyl-3-buten-2-one (I) The crystals (12 g.) melting at 211~213° were suspended in a mixture of conc. hydrochloric acid (20 cc.) and water (40 cc.), and heated for a brief time in the water-bath. The liberated oil, on extraction with ether, dehydration over calcium chloride and fractionation, gave a pale yellow oil (7 g.) distilling at 124°/19 mm. This sweet smelling ketone did not solidify at room temperature, and colourised on standing. Found: C, 71.53, H, 6.55. Calcd. for $C_9H_{10}O_2$: C, 71.96, H, 6.71%.

This ketone (1 g.) was suspended in sodium hypochlorite solution[1] (10 cc.) and the vessel kept in water at ordinary temperature for 2 days, with occasional shaking. The resulting chloroform was removed and the aqueous solution acidified with dilute hydrochloric acid to yield α-methyl-2-furanacrylic acid (III) (0.6 g.).

This ketone (2 g.) was refluxed with conc. hydrochloric acid (1.5 cc.) and alcohol (5 cc.) on the water-bath for 3 hrs. The reaction mixture, worked up in the same manner as previously reported,[1] did not give any dioxocarboxylic acid.

1-(2-Furyl)-1-penten-3-one (II) A semicarbazone mixture (12 g.) of the needle crystals (m.p. 183~184°) and tabular crystals (m.p. 166~167°) was treated with dilute hydrochloric acid in the same manner as in the case of 4-(2furyl)-3-methyl-3-buten-2-one (I) to give a pale yellow oil (7 g.) distilling at 126°/19 mm. This sweet smelling ketone also did not solidify at room temperature and colourised on standing. Found: C, 71.34, H, 6.57. Calcd. for $C_9H_{10}O_2$: C, 71.96, H, 6.71%.

This ketone, on suspencion in sodium hypochlorite solution at room temperature for 2 days, did not undergo any reaction.

This ketone (2 g.) was refluxed with conc. hydrochloric acid (1.5 cc.) and alcohol (5 cc.) for 3 hrs. in the water-bath. The reaction mixture, worked up in the same manner as previously reported, gave the dioxocarboxylic acid (0.8 g.) melting at 83~84° which was considered to be γ, ζ-dioxopelargonic acid (IV).

Summary

From the condensation product of furfural with methyl ethyl ketone by aqueous sodium hydroxide were isolated 4-(2-furyl)-3-methyl-3-buten-2-one (I) and 1-(2-furyl)-1-penten-3-one (II).

The former ketone (I) was oxidised by sodium hypochlorite to yield α-methyl-2-furanacrylic acid, (III) but gave no γ, ζ-dioxo-ε-methylcaprylic acid by refluxion with alcoholic hydrochloric acid.

The latter ketone (II) gave γ, ζ-dioxopelargonic acid (IV) by refluxion with alcoholic hydrochloric acid, but was no acted upon by sodium hypochlorite.

The semicarbazone of 1-(2-furyl)-1-penten-3-one (II) existed in two forms of the needle crystals melting at 183~184° and the tabular crystals melting at 166~167°.

The author expresses his sincere thanks to Dr. T. Hayashi for his kind advice.

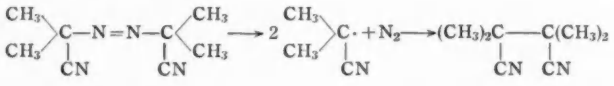
Scientific Research Institute, Komagome, Bunkyo-ku, Tokyo

The Dimerization of Trichloroethylene Induced by the Decomposition of α, α'-Azodiisobutyronitrile and the Structure of the Dimer

By Osamu SIMAMURA and Naoki INAMOTO

(Received December 14, 1953.)

α, α'-Azodiisobutyronitrile first prepared by Thiele and Heuser[1] decomposes thermally to give tetramethylsuccinonitrile and nitrogen, involving homolysis to intermediate radicals $(CH_3)_2\dot{C}CN$:



It acts therefore as a powerful initiator of the vinyl polymerization. The synthetical aspects of the chemistry of this and related compounds pertaining to this property have been reviewed by Ziegler[2]. The thermal decomposition of these compounds and the chemical nature of the radicals thereby produced have recently been the subject of numerous investigations[3]. It appeared to be of interest, as part of a study of chemical behavior of radicals in solution, to investigate the decomposition of α, α'-azodiisobutyronitrile in trichloroethylene which is known to give no high polymeric substances except in copolymerization with other reactive monomers[4]. In the present paper an account is given of the determination of the structure of the dimer of trichloroethylene produced by the agency of α, α'-azodiisobutyronitrile, and a mechanism of the dimerization is proposed.

By boiling trichloroethylene with 1 to 1.5 mole % of α, α'-azodiisobutyronitrile added in portions over a period of 35 to 64 hours and fractionating the reaction mixture a dimer, $C_4H_2Cl_6$, of trichloroethylene was obtained as a main product in 25 to 28% conversion (see Table I). The fractionation of higher polymeric products was not carried out, and the ratio of the weight of the dimer obtained to the weight of the residue from the distillation was shown in the column headed "Dimer/Polymers" in Table I. As Frank and Blackham[5] had reported the dimerization of trichloroethylene by means of dibenzoyl peroxide, we also repeated their experiment and the dimerized product was shown to be identical with that obtained by the action of α, α'-azodiisobutyronitrile by comparing their infrared spectra (see Fig. 1 and Table II).

TABLE I

DIMERIZATION OF TRICHLOROETHYLENE

Expt. No.	C_2HCl_3 g.	Azodinitrile mole %	Benzoyl peroxide mole %	Reaction time hrs.	Yield of dimer g.	B.p. °C/mm. Hg	Conversion %	Dimer/Polymers
1	131	1.5		35.5	27	103–5/10	25.3	4.4
2	168	1.0		38	31	117–8/18	24.5	3.0
3	320	1.0		64	79.5	111–3/12	28.3	7.3
4	240		1.0	41	120	98–100/7–8	58.3	6.0
Data from ref. 5			1.2	95		104.4/10	68.3	9.0

TABLE II

PROPERTIES OF DIMER $C_4H_2Cl_6$

Source	B.p. °C/mm. Hg*	d_4^{20}	n_D^{20}	MR_D
Expt. 3	104/10	1.6786	1.5452	49.51
Expt. 4	98–100/7–8	1.6727	1.5471	49.72
Ref. 5	104.4/10	1.6760	1.5461	49.66
				Calcd. 49.41

* Redistilled.

1) J. Thiele and K. Heuser, *Ann.*, **290**, 1 (1896).
2) K. Ziegler, *Brennstoff-Chem.*, **30**, 181 (1949).
3) See *Ann. Rep. on Progr. Chem.*, **49**, 115 (1952).
4) K. W. Doak, *J. Am. Chem. Soc.*, **70**, 1525 (1948).
5) C. E. Frank and A. U. Blackham, ibid., **72**, 3283 (1950).

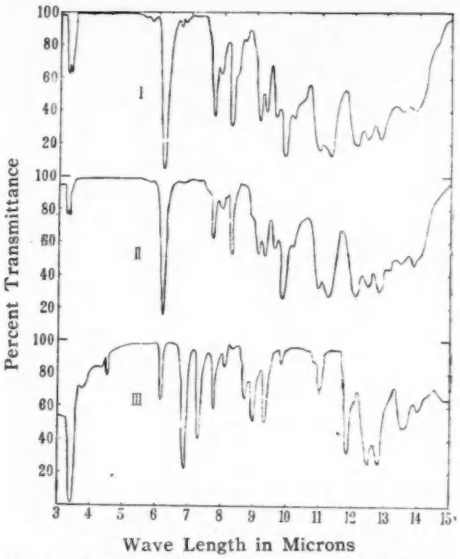
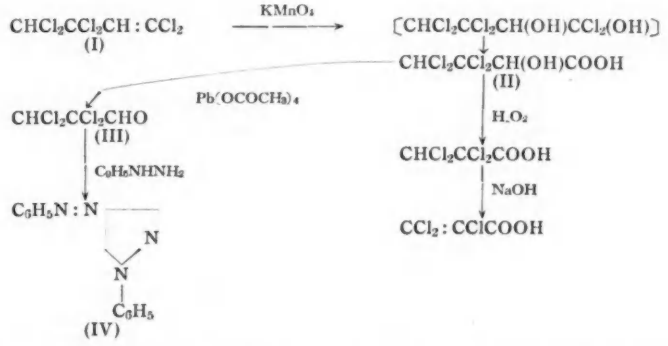


Fig. 1. Infrared absorption spectra of trichloroethylene dimers (I and II) obtained in the presence of azodiisobutyronitrile and dibenzoyl peroxide, respectively, and of 1, 1, 3, 3, 4-pentachloro-5-cyano-5-methyl-1-hexene(III).

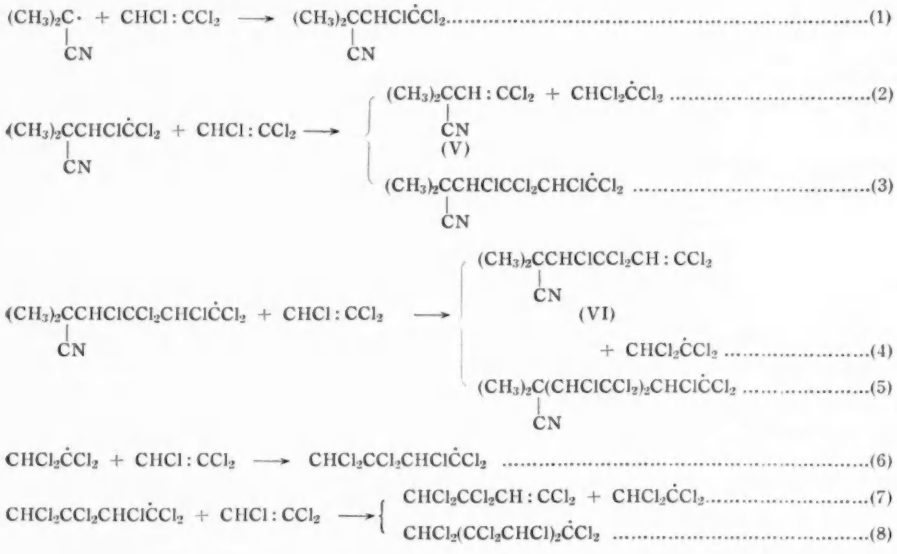
The chemical constitution of the dimer of trichloroethylene (I) was established to be 1, 1, 3, 3, 4, 4-hexachloro-1-butene on the basis of the following degradations (see the annexed scheme). The oxidation of the dimer with potassium permanganate in cold aqueous acetone gave a crude acid (II), but it could be neither crystallized nor distilled without decomposition, and no attempt at characterization was therefore made. It was shown, however, that it is an α-hydroxy acid, because, in the first place, the action of the Fenton reagent[6] converted it to an acidic substance which gave a reddish brown precipitate with 2, 4-dinitrophenylhydrazine showing that an α-keto acid was formed, and secondly, on oxidation with lead tetraacetate according to Oeda[7], it gave an aldehyde (III). This aldehyde also was not isolated in a pure state, but it developed a purple color with Schiff's reagent and gave with excess phenylhydrazine 1-phenyl-4-phenylazopyrazole (IV), m. p. 126–7°, demonstrating that the aldehyde (III) contains three carbon atoms. The formation of the pyrazole from aldehyde III, which must be 2, 2, 3, 3-tetrachloropropanal, as will be seen below, is readily understandable from its structure; for α and β carbon atoms of the aldehyde carry respectively two chlorine atoms and their function may therefore be equivalent to a carbonyl group. The same pyrazole is obtained by the action of phenylhydrazine on compounds with analogous structural features, namely, 1, 1, 3, 3-tetrachloropropanone[8] and 1, 3-bisphenylhydrazone of propanonedial[9]. By heating the crude hydroxy acid (II) with 30% hydrogen peroxide 2, 2, 3, 3-tetrachloropropanoic acid, m. p. 79–80°, was obtained, which was dehydrochlorinated to 2, 3, 3-trichloropropenoic acid, m. p. 75–6°, by heating with aqueous sodium hydroxide. Thus, the grouping $CHCl_2CCl_2$- must be present in the dimer molecule and the double bond is accordingly located at the terminal position, the structure of the dimer having to be either $CHCl_2CCl_2CH:CCl_2$ or $CHCl_2CCl_2CCl:CHCl$. That the former structure is the correct one is shown by the formation of the three-carbon aldehyde (III) by the two-step cleavage of the double bond, which requires that carbon atom 2 of the dimer must bear a hydrogen atom. The structure of the hydroxy acid (II) must be 2-hydroxy-3, 3, 4, 4-tetrachlorobutanoic acid which is derived from the dimer (I) by hydroxylation at the double bond followed by hydrolysis and dehydration at carbon atom 1.



6) H. J. H. Fenton and H. O. Jones, *J. Chem. Soc.*, **77**, 71 (1900).
7) H. Oeda, This Bulletin, **9**, 8 (1934).
8) S. Levy and F. C. Witte, *Ann.*, **252**, 345 (1889); Th. Zincke and O. Kegel, *Ber.*, **22**, 1478 (1889).
9) H. v. Pechmann and L. Vanino, *Ber.*, **27**, 222 (1894).

Henne and Ruh[10] had attempted the determination of the structure of the trichloroethylene dimer obtained by means of dibenzoyl peroxide, but they could not decide between several possibilities. Frank and Blackham,[5] without presenting any experimental proof, had inferred the same structure as above by assuming that the dimerization of trichloroethylene follows a similar course to those of chlorinated olefins the structures of whose dimers are well established.[11,12] Since the identical dimer is obtained from trichloroethylene, as has been mentioned earlier, by means of either benzoyl peroxide or α, α'-azodiisobutyronitrile, the present structural proof is valid also for the dimers obtained by the American workers.

The residue from the fractionation of the dimer (Expt. No. 3) yielded a small amount of a new crystalline compound, m. p. 167–168°, which analyzed for $C_8H_8Cl_5N$ (see Fig. 1 for the infrared spectrum). In view of the established structure of the dimeric product and of the initiation of this reaction by α, α'-azodiisobutyronitrile, it is highly probable that this compound is 1, 1, 3, 3, 4-pentachloro-5-cyano-5-methyl-1-hexene (VI), which should result from the successive addition of 1-cyano-1-methylethyl radical produced from an initiator molecule to two molecules of trichloroethylene followed by loss of a chlorine atom (reactions 1, 3 and 4 shown in the following scheme). The isolation of the compound $C_8H_8Cl_5N$ is significant in that, in the first place, it contains a radical moiety from the initiator molecule, thus demonstrating the mechanism of the initiation, and further, it affords an experimental proof of the chlorine atom being transferred from a growing radical chain to a molecule of trichloroethylene, a new chain being thereby initiated. Thus, we are led to formulate the initiation, propagation and termination of the dimerization as follows:



In the above formulation the transference of the chlorine atom is shown as occurring by a collision between a radical and a molecule of trichloroethylene. However, the possibility could not be excluded experimentally that the transference is effected by initial decomposition of the radical into a stable molecule and a chlorine atom, the latter adding subsequently to a molecule of trichloroethylene to give radical $CHCl_2\dot{C}Cl_2$.

A search for 1, 1-dichloro-3-cyano-3-methyl-1-butene (V) failed, the formation of which should be expected from the mode of initiation and the comparative ease of transference of the chlorine atom to trichloroethylene. Reactions 5 and 8 giving rise to higher polymeric products are of subordinate importance, as is seen from the last column in Table I, in line with the observation that trichloroethylene is unable to give high polymeric

10) A. L. Henne and R. P. Ruh, *J. Am. Chem. Soc.*, **69**, 279 (1947).
11) K. E. Wilzbach, F. R. Mayo and R. Van Meter, ibid., **70**, 4069 (1948).
12) M. S. Kharasch and G. Büchi, *J. Org. Chem.*, **14**, 84 (1949).

substances on account of the steric hindrance exerted by the chlorine atoms at the double bond.

The dimerization by a chain transer reaction in which a halogen atom is transferred from the dimer radical to the monomer has originally been suggested by Wilzbach and Mayo[11] for methallyl chloride, and Kharasch and Büchi[12] explained the formation of 5-bromo-4-(bromomethyl)-1-pentene in the decomposition of acetyl peroxide in allyl bromide on the basis of a similar mechanism. The present study has brought foward another case in which such a mechanism is operative.

Experimental

Materials α, α'-Azodiisobutyronitrile was prepared according to Thiele and Heuser[13], and recrystallized from ether, m. p. 104° with decomposition. Commercial trichloroethylene was washed with aqueous potassium carbonate and then with water, dried with calcium chloride and fractionated. A fraction boiling at 87.0° was used.

Dimerization To boiling tricholoroethylene under reflux 1 to 1.5 mole % of α, α'-azodiisobutyronitrile was added in portions over a period of 35 to 64 hours, towards the end of which the temperature of the heating bath had to be elevated to 135° to keep the liquid refluxing. The results of three runs are shown in Table I. A reaction mixture, on cooling, deposited tetramethylsuccinonitrile (e.g., 0.14 g. in Expt. No. 3), m.p. 169°; the filtered solution was repeatedly fractionated through a Vigreux column 50 cm. in length; unreacted trichloroethylene was recovered and the dimer distilled over at 104° at 100 mm. Hg (Found: C, 18.7; H, 1.0; Cl, 80.86. Calcd. for $C_4H_2Cl_6$: C, 18.3, H, 0.8; Cl, 80.99%.). The residue from the fractionation, treated with ether, deposited 0.4 g. of 1, 1, 3, 3,4-pentachloro-5-cyano-5-methyl-1-hexene (VI), m. p. 167–8° (from alcohol) (Found: C, 32.7; H, 2.6; N, 4.73; Mol. wt. (Rast), 296. Calcd. for $C_8H_9Cl_5N$: C, 32.5; H. 2.7; N, 4.74%; Mol. wt., 295.5). When the mother liquor was subjected to distillation at 0.04 mm. Hg., 5.6 g. of unidentified viscous oil (probably a trimer etc.) passed over at 122–124°, from which a further 0.3 g. of the pentachlorocyanomethylhexene crystallized out.

Degradation of the Dimer Potassium permanganate (6.5 g.) was added in portions with shaking to 5.0 g. of the dimer dissolved in 30 cc. of acetone and 5 cc. of water cooled with water at 10°. The mixture was filtered from the manganese dioxide, which was then washed with acetone. The filtrate and the washing were combined and evaporated on a water bath. The residue was neutralized with hydrogen sodium carbonate, the solution evaporated under diminished pressure of a water pump, and the residue extracted with ether to remove neutral substances. It was acidified with dilute hydrochloric acid and saturated with sodium chloride, and the solution was extracted repeatedly with ether. The ethereal extracts were combined and dried with anhydrous sodium sulfate and the ether was removed on a water bath giving 2.5 g. of a liquid residue comprising 2-hydroxy-3, 3, 4, 4-tetrachlorobutanoic acid (II), which could not be brought to crystallization by keeping over concentrated sulfuric acid in an evacuated desiccator for seven days.

To the crude α-hydroxy acid (II) (2.0 g.) in 5 cc. of water heated in a boiling water bath 30% hydrogen peroxide was added drop by drop over a period of one hour until the presence of its excess was shown by potassium iodide-starch paper. The reaction mixture was cooled and extracted with ether and the ether removed. The liquid residue (1.2 g.), on being kept over concentrated sulfuric acid in an evacuated desiccator for three days, deposited 0.3 g. of hygroscopic crystals of 2, 2, 3, 3-tetrachloropropanoic acid, m. p. 79–80° (from petroleum ether, reported m. p. 76°[13]) (Found: Cl, 66.63; neutralization equivalent, 222. Calcd. for $C_3H_2Cl_4O_2$: Cl, 66.98%; neutralization equivalent, 212). Further crops of the acid (a total of 0.8 g.) were obtained after several days. This acid (1 g.) was heated with 0.4 g. of sodium hydroxide in 5 cc. of water, the mixture acidified with hydrochloric acid and extracted with ether, the ether removed and the residue recrystallized from petroleum ether to give 0.8 g. of 2, 3, 3-trichlropropenoic acid, m. p. 75–6° (reported m. p. 76°[14]) (Found: neutralization equivalent, 182.5. Calcd. for $C_3HCl_3O_2$: 175.5).

To a stirred solution of 0.5 g. of the α-hydroxy acid (II) in 25 cc. of benzene at 60–80° lead tetraacetate was added in portions until the oxidizing power began to persist in the solution (potassium iodide-starch paper). It took about one hour. The excess lead tetraacetate was destroyed by heating for 30 minutes with anhydrous oxalic acid. The benzene solution developed a purple color with Schiff's reagent. It was distilled on a water bath to remove benzene, the residue added with 30 cc. of alcohol and filtered. The filtrate was heated with 2 g. of phenylhydrazine, some precipitate filtered off, and the filtrate concentrated on a water bath to give golden yellow crystals of 1-phenyl-4-phenylazopyrazole, m. p. 126–7° (from alcohol, yield 50 mg.) (Found: N, 22.9. Calcd. for $C_{15}H_{12}N_4$: 22.57%).

Infrared Data The infrared spectra were recorded on a Baird Double Beam Spectrophotometer equipped with rock salt optics. They were shown in Fig. 1. The spectrum of 1, 1, 3, 3, 4-pentachloro-5-cyano-5-methyl-1-hexene suspended in liquid paraffin shows an absorption band of the nitrile group at 4.5 μ and that of the ethylenic bond at 6.13 μ.

Summary

1. Trichloroethylene has been dimerized by

13) C. F. Mabery and A. W. Smith, *Ber.*, **22**, 2659 (1889).
14) J. Böeseken and P. Dujardin, *Rec. trav. chim.*, **32**, 97 (1913).

boiling with α, α'-azodiisobutyronitrile to $C_4H_2Cl_8$, which has been identified as 1, 1, 3, 3, 4, 4-hexachloro-1-butene by degradation.
2. A compound of molecular formula $C_8H_8Cl_7N$, whose structure is presumably 1, 1, 3, 3, 4-pentachloro-5-cyano-5-methyl-1-hexene, has been isolated. This fact indicates that the reaction is initiated by the addition of 1-cyano-1-methylethyl radical to trichloroethylene and propagated by the transference of a chlorine atom from the dimeric radical to a molecule of the monomer.
3. The decomposition of dibenzoyl peroxide in trichloroethylene gives the same dimer as above, the structural identity being confirmed infrared spectrometrically.

The authors' thanks are due to Dr. H. Kamada and Mr. S. Tanaka, Engineering Research Institute, for measuring the infrared spectra and to the Ministry of Education for a Grant-in-Aid for Scientific Research.

Department of Chemistry, Faculty of Science, Tokyo University, Tokyo

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Spectrochemical Study of Microscopic Crystals. V. Relation between Dichroism and Direct Interaction between Metal Atoms in the Crystals of Bis (Dimethylglyoximo)-Copper (II), Nickel (II) and Platinum (II)[1]

By Shoichiro YAMADA and Ryutaro TSUCHIDA

(Received December 24, 1953)

In the earlier papers the present authors reported on the dichroism of those complex compounds which exhibit unusually deep colours in the crystalline state as compared with those in solution, and concluded that in the crystals of Magnus's green salt[2] and salts of tetracyanoplatinate (II)[3] there exists direct interaction between the central platinum atoms of planar complexes, which are arranged in such a way that they are piled one just above and below another. Recently Godycki and Rundle[4] reported on the crystal structure of bis (dimethylglyoximo)-nickel (II) and suggested the possibility of a direct, though weak, interaction between nickel atoms. They also asserted that the pleochroism of the crystal supported the above assumption, but gave no experimental value for the absorption coefficients. Moreover, their descriptions of the dichroism contradict our measurements, though the conclusion arrived at through their argument on the basis of their qualitative observation happens to be similar to ours. In this paper we report on the quantitative dichroism measurement of the crystals of bis (dimethylglyoximo)-copper (II), nickel (II) and platinum (II), and discuss the relation between the dichroism and the state of the complex molecules in these crystals.

Experimental

Materials. Bis (dimethylglyoximo) Copper (II) Black monoclinic prisms were obtained from solutions of copper acetate and of dimethylglyoxime in 50% alcohol. The crystal is remarkably dichroic; it appears to be dark reddish brown with linearly polarized light having its electric vector along the c-plane, the c-axis being the needle axis, and brownish yellow with that having its electric vector perpendicular to the c-plane. The Dichroism measurement was made with reference to the above two directions.

Bis (dimethylglyoximo) Nickel (II) The compound was prepared from an aqueous solution of nickel sulphate and an alcoholic solution of dimethylglyoxime, and recrystallized from chloroform. Red acicular crystals of orthorhombic system were obtained. A distinct dichroism was observed with a thin crystal under the microscope; the crystal appears red with linearly polarized light having its electric vector parallel to the needle axis, and orange with that having its electric vector perpendicular to the axis. The measurement was made in reference to these two directions.

Bis (dimethylglyoximo) platinum (II) Chocolate-coloured acicular crystals were prepared from an aqueous solution of potassium tetrachloroplatinate (II) and an alcoholic solution of dimethylglyoxime.[5] The crystal is strongly dichroic; it appears greenish black with the electric vector

1) Read before the meeting of the Symposium on Coordination Compounds, Nagoya, Japan, November 8, 1953.
2) R. Tsuchida and S. Yamada, *J. Chem. Soc. Japan*, **70**, 44 (1949); S. Yamada, *J. Am. Chem. Soc.*, **73**, 1579 (1951).
3) S. Yamada, This Bulletin, **24**, 125 (1951).
4) L. E. Godycki and R. E. Rundle, *Acta Cryst.*, **6**, 478 (1953).
5) Gmelins Handbuch der anorg. Chem., 7. Aufl., Band 5, 1915, p. 604.

parallel to the needle axis, and orange with the electric vector perpendicular to the above. The dichroism measurement was per formed on the prism face in the above mentioned directions.

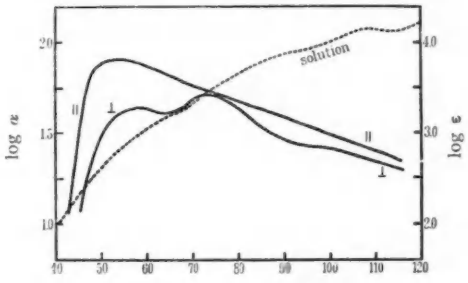
Measurements.—Quantitative dichroism measurement of the crystals was performed by the Tsuchida-Kobayashi's microscopic method.[6] α denotes absorption coefficient per mm. of a crystal. Molecular absorption coefficients of a crystal, k, were calculated from the relation, $k=10\alpha M/\rho$, where M and ρ represent molecular weight of the compound and density of the crystal, respectively.

Absorption spectra were obtained with a Beckman DU spectrophotometer in a chloroform solution of the nickel compound, and in an alcoholic solution of the copper compound. Extinction coefficients, ε, are given by the following expression, $\varepsilon=1/\text{cd}\cdot\log(I_0/I)$.

$\parallel$-or $\perp$-absorption means absorption of light with the electric vector parallel or perpendicular to the plane of the molecule, respectively.

Results and Discussion

Bis (dimethylglyoximo) copper (II) Results of the measurement are shown in Fig. 1, and tabulated in Table I. The crystal



Frequency (ν), 10^{13}/sec.

Fig. 1. Absorption spectra of bis (dimethylglyoximo) copper (II).

structure analysis was reported by Bezzi et al.[7] According to their results, the planes of the planar molecules are parallel to each other and als to othe c-plane of the crystal. That is, the absorption spectrum with the electric vector along the c-plane corresponds to the $\parallel$-absorption and the absorption with the electric vector perpendicular to the c-plane corresponds to the $\perp$-absorption.

TABLE I

ABSORPTION MAXIMA OF BIS (DIMETHYLGLYOXIMO) COPPER (II)

	10^{13}/sec. ν	$\log\alpha$	k
$\parallel$-abs.	54	1.91	182×10^3
$\perp$-abs.	58	1.64	98×10^3

$\Delta\nu=4\times10^{13}$/sec., $\Delta\log\alpha_{max}=0.27$, $\alpha_\parallel:\alpha_\perp=1.86:1$.

It has been known that complexes of copper (II), in general, show in the visible or infrared region an absorption band which can be ascribed to the linkages between the metal and the ligands. Comparing the absorption curves of copper-dimethylglyoxime with those of other cupric complexes, the band at $\nu=58\times10^{13}$/sec. (Band A) for the $\perp$-absorption is considered as due to the linkages between copper and the ligands. Most metallic compounds with dimethylglyoxime or similar compounds,[8,9] which have π-electron system, exhibit absorption curves of complicated structure and also a band which can be supposed to be originated from $d\pi$ interaction between d-electrons of a transition metal atom and electrons of a ligand.[10] Thus the band at $\nu=73.2\times10^{13}$/sec. (Band B) is tentatively assumed to be of a similar nature to the above band associated with $d\pi$ interaction.

The $\parallel$-absorption shows only a flat curve without a definite peak; it may be a superposition of the band A and band B.

With the absorption band A, the following regularity on the dichroism is obtained: *the $\parallel$-absorption is bathochromic and hyperchromic to the $\perp$-absorption.* The relation is similar to that which had been induced previously with planar quadri-coordinated complexes of transition metals,[11,12] and therefore can be understood in the same way as previously reported. Thus, since the electric moment associated with the linkage between copper and nitrogen atoms should be larger in the direction along the complex plane than in the direction perpendicular to the plane, $\parallel$-absorption is expected to be hyperchromic to the $\perp$-absorption. This was found to be the case with the cupric complex. Hence,

6) R. Tsuchida and M. Kobayashi, "The Colours and the Structures of Metallic Compounds," Zoshindo, Osaka, Japan, 1944, p. 180. See also the previous papers of this series.

7) S. Bezzi, E. Bua and G. Schiavinato, *Gazz. Chim. Ital.*, **81**, 856 (1951).

8) Some of curves are found in Ref. 6, p. 194.

9) Data with cobaltic compounds are given in H. Kuroya, *J. Inst. Polytech. Osaka City Univ.*, **1**, 11 (1951).

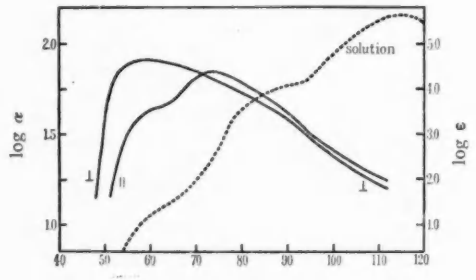
10) P. Krumholz, *J. Am. Chem. Soc.*, **75**, 2163 (1953), etc.

11) About palladium (II) and platinum (II) complexes, see S. Yamada, *J. Am. Chem. Soc.*, **73**, 1182 (1951); S. Yamada and R. Tsuchida, This Bulletin, **23**, 439 (1953).

12) About cupric complexes, to be published later.

the dichroism indicates that the molecules in this crystal exist as independent units, in agreement with the result of the crystal structure analysis.[7]

Bis (dimethylglyoximo) nickel (II) Results of the measurement are shown in Fig. 2, and tabulated in Table II. According to



Frequency (ν), 10^{13}/sec.

Fig. 2. Absorption spectra of bis (dimethylglyoximo) nickel (II).

the crystal analysis by Godycki et al.,[4] the planes of the complexes are parallel to each other and perpendicular to the c-axis, with the nickel atoms situated on lines along the c-axis. As in the case of the corresponding copper complex, it is supposed that the band of the ∥-absorption with its maximum at $\nu=60\times10^{13}$/sec. (Band A) is originated from transitions directly related to the linkages between the metal and the co-ordinating atoms, and that the band (Band B) with its maximum at $\nu=74\times10^{13}$/sec., which is reasonably considered as corresponding to the band at $\nu=86\times10^{13}$/sec. with the solution, may be due to the specific $d\pi$ interaction between the metal with d-electrons and atoms of the ligands with π-electrons. Instead of the two distinct bands in the ∥-absorption, only a broad absorption band is observed in the ⊥-absorption; in the latter both the bands would come so close together that only superposition of them may be observed. As to the band A, which has been assumed to

TABLE II

ABSORPTION MAXIMA OF BIS (DIMETHYLGLYOXIMO) NICKEL (II)

	10^{13}/sec. ν	log α	k
∥-abs.	61	1.63	76×10^3
⊥-abs.	59	1.91	144×10^3

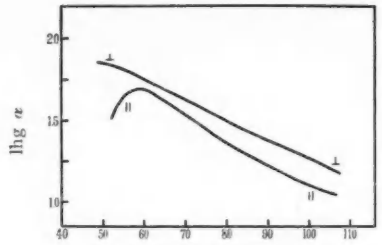
$\Delta\nu=2\times10^{13}$/sec., $\Delta\log\nu_{max}=0.28$, $\alpha_{\parallel}:\alpha_{\perp}=0.53:1$.

be ascribed to the co-ordination linkages, there can be found the following relation: *the ⊥-absorption is by far hyperchromic to the ∥-absorption.* The relation is reverse to those observed with the corresponding copper compound, and also with metallic planar complexes of the normal type, that is, the type without the interaction between adjacent molecules.[11,12] The above relation that the electric vector perpendicular to the complex plane is more strongly absorbed than the vector along the plane indicates that the planar complexes are under some effect in the direction perpendicular to the planes of the complex molecules, and that the effect must be of such a nature as to cause a direct influence on the co-ordination linkages.

Such an effect would be considered to be a direct interaction between the nickel atoms which are arranged one just above and below another. Godycki et al.[4] also suggested, on the basis of their erroneous observation, similar interaction in this compound; their observation that the electric vector is more strongly absorbed along the plane of the complex than in the direction perpendicular to the plane is quite incomprehensible and seems incorrect.

Interactions between π-electrons might be considered besides the metal-metal interaction. However, since the complex molecules piled above and below one another are rotated about ninety degrees with respect to each other, the interaction between the π-electron systems of adjacent molecules may be ruled out. It is also probable that π-π interaction between the nitrogen atoms may contribute to this result to some extent, judging from the distance between nitrogen atoms of adjacent molecules. It seems reasonable, however, to consider that the motal-metal interaction should be dominant, compared with the contribution of the π-π interaction.

Bis (dimethylglyoximo) platinum (II) Results of the measurement are shown in Fig. 3. The crystal structure analysis of the compound has not been reported. However, judging from the crystal structure of the corresponding nickel and palladium compounds,[4] it is probably certain that the complex planes in the platinum (II) compound are parallel to each other and perpendicular to the needle axis, just as in the case of the other two. On the basis of the above assumption was assigned the ∥-and ⊥-absorp-



Frequency (ν), 10^{12}/sec.

Fig. 3. Absorption spectra of bis (dimethylglyoximo) platinum (II).

tion. Since the ⊥-absorption stretches out beyond the region of measurement, the maximum could not be determined. It is seen that the crystal of the platinum-dimethylglyoxime compound shows its absorption in the extraordinarily long wave-length region, in comparison with other platinum compounds such as potassium tetrachloro-, tetrabromo-,[11,13] and dioxalato-[14] platinate (II), and others. This suggests that some effect might be exerted upon the planar molecules in the former compound. Further, by inspecting the dichroism, the following relation is found: *the ⊥-absorption is much more hyperchromic and bathochromic than the ∥-absorption.* The above relation is reverse to that in case of complexes of the normal type. The reversal of the effect as to the dichroism indicates that the effect, which has direct influence on the absorption closely connected with the linkages between the metal and the ligands, should be taken into consideration. Hence, as in the case of the corresponding nickel compound, a direct interaction is supposed to exist between platinum atoms.

The Nature of the Metal-Metal Interaction The metal-metal interaction as proposed in the nickel-and platinum-dimethylglyoxime compounds is considered to be of a similar nature to the interaction which was previously reported by the present authors in the case of Magnus's green salt[2] and salts of tetracyano-platinate (II).[3] In order to explain the metal-metal interaction in the latter crystals, the following assumption was presented in the former report.[2,3] In the quadri-coordinated planar complexes of platinum (II), four atoms of the ligands with two pairs of electrons around the central metal form octahedral hybridization.[15] The pairs of electrons above and below platinum cores of the complexes exert mutual effects upon one another, overlapping of electronic density being naturally expected (Fig. 4).

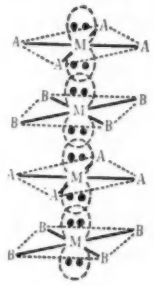


Fig. 4. Metal-metal interaction in the Magnus's type compounds.

The same assumption may apply to the crystal of the nickel (II)-and platinum (II)-dimethylglyoxime compounds. When the above metal-metal interaction is getting stronger, the overlapping of the electrons may also become larger. In other words, the greater the overlapping of the electrons, the more the sharing of electrons. In the extreme structure, in which the overlapping might reach the extremity, complete sharing of electrons might happen (Extreme structure II in Fig. 5).[16] It may be reasonably sup-

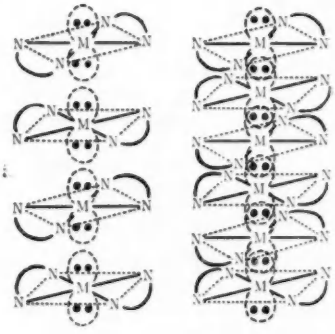


Fig. 5. Extreme structures of some metallic dimethylglyoximo compounds involving metal-metal interaction.

posed that the more stable the extreme structure, the larger would be the overlapping and the greater the contribution of the structure would result, in which sharing of the electrons is complete. It is to be noted that the metal-metal interaction of the said type has been found mostly with the compounds

13) S. Yamada, H. Yoneda and R. Tsuchida, *J. Chem. Soc., Japan.* **69**, 145 (1948).

14) R. Tsuchida and S. Yamada, unpublished.

15) About the possibility of octahedral hybridization in quadri-coordinated planar complexes, see, for example, R. Tsuchida, M. Kobayashi and H. Kuroya, *Rev. Phys. Chem. Japan*, **13**, 158 (1939).

16) The contribution of the extreme structure, in which complete sharing of an electron pair occurs, was recently pointed out by Godycki et al. (Ref. 4).

of Ni (II), Pd (II) and Pt (II). In order to explain such tendency, we wish to propose the following hypothesis: *When complete sharing of electrons would occur between complex molecules arranged above and below one another (structure II), Ni (II), Pd (II) and Pt (II) would attain the effective atomic number of the rare gases and thereby the extreme structure II (Fig. 5) might be stabilized.* Thus the larger contribution of the extreme structure II, and hence the greater stability of the metal-metal interaction, could be explained in terms of the above hypothesis with Ni (II), Pd (II) and Pt (II) compounds.

The same assumption applies satisfactorily also to the stability of the molecule of copper acetate, $Cu_2(CH_3CO_2)_4 \cdot 2H_2O$,[17] in which, according to the above hypothesis, the copper atoms in the extreme structure would attain the effective atomic number of krypton by sharing one pair of electrons between two copper atoms.

Summary

Dichroism of the crystals of bis (dimethylglyoximo)-copper (II), nickel (II) and platinum (II) has been quantitatively determined by the microscopic method in the region from 2400 to 7000 Å.

The crystal of the copper compound has been found to show dichroism of the normal type, indicating that no specific metal-metal interaction can be expected in this crystal.

The crystals of the nickel (II) and platinum (II) compounds exhibit anomalous dichroism. It has been concluded that in these crystals there should exist metal-metal interaction.

A hypothesis has been presented, in order to explain the tendency that the specific metal-metal interaction similar to that proposed above has been found mostly with Ni (II), Pd (II) and Pt (II) compounds.

The authors wish to thank Mr. E. Hongo of Nisshin Chemicals Co. for his help in the experimental work and the Analytical Laboratory of our department for measurement of absorption spectra in solution. Thanks are also due to the Ministry of Education for a grant.

Department of Chemistry, Faculty of Science, Osaka University, Nakanoshima, Osaka

17) About the configuration of the molecule, see J. N. van Niekerk and F. R. L. Schoening, *Acta Cryst.*, **6**, 227 (1953).

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*Dipole Moments of Cyclic Siloxanes and Thiosiloxanes**

By Yukio KURITA and Michio KONDO

(Received December 25, 1953)

Introduction

The molecular structures of cyclic siloxanes have been studied in various ways, especially by electron diffraction[1,2] and by X-ray study[3]. Although Sauer and Mead[4] calculated the dipole moments of several cyclosiloxanes from the dielectric measurements on pure liquids, they did not discuss the configuration in detail. The physicochemical studies of cyclothiosiloxanes have not yet been carried out extensively, but Yokoi and Nomura[5] have made electron diffraction studies on these compounds.

The measurement of the dipole moments of these compounds in nonpolar solvents seemed to be desirable to elucidate the geometrical configurations and atomic polarizations of these compounds as well as the polarity of Si-O and Si-S bonds. Hence we measured the dipole moments of hexamethyldisiloxane, two cyclosiloxanes, and two cyclothiosiloxanes in benzene solution.

Experimental

The materials used were kindly given to us by Mr. M. Yokoi of Nagoya University. They are:

I. Hexamethyldisiloxane. b.p. 98°.
II. Hexamethylcyclotrisiloxane. m.p. 64.5°, b.p. 135°.
III. Octamethyltetracyclosiloxane. m.p. 17.4°, b.p. 171°.

* Read before the Annual Meeting of the Chemical Society of Japan held on April 4, 1953.

1) E. H. Aggerwal and S. H. Bauer, *J. Chem. Phys.*, **18**, 42 (1950).
2) M. Yokoi, (to be published shortly).
3) L. K. Frevel and M. J. Hunter, *J. Am. Chem. Soc.*, **67**, 2275 (1945).
4) R. O. Sauer and D. J. Mead, *J. Am. Chem. Soc.*, **68**, 1794 (1946).
5) M. Yokoi and T. Nomura, (to be published shortly).

IV. Tetramethylcyclodithiosiloxane*. m. p. 105.5°, b.p. 172–3°.
V. Hexamethylcyclotrithiosiloxane*. m. p. 17–8°, b.p. 151.5–3.5°
(38 mm. Hg.)

The apparatus and the method of measurements were the same as given already in our previous paper[6]. For the calculation of $P_{2\infty}$, we used a modified Hedestrand's method[7]. The results are shown in Table I. The values of P_0+P_A of these compounds are not very large, and the calculated moments therefore depend sensitively upon the assumed values of P_A. The values in Table I are considered to be most reasonable, as will be discussed in the following.

TABLE I

DIPOLE MOMENTS OF CYCLOSILOXANES AND CYCLOTHIOSILOXANES IN BENZENE SOLUTION

	temp.	ε_1	d_1 (g./cc.)	α	(g./cc.)	$P_{2\infty}$ (cc.)	R_D	P_A	μ(D)
I	20°	2.2845	0.87610	0.13	−0.12	67.1	48.9	4.9=0.1R	0.80
II	30°	2.2632	0.86642	−0.070	0.047	66.7	55.8	10.9=0.2R	0.0
III	25°	2.2750	0.87114	0.11	0.082	98.1	74.5	14.5=0.2R	0.67
IV	30°	2.2652	0.86554	0.348	0.133	64.3	55.3	9.0	0.0
V	20°	2.2839	0.87635	0.804	0.162	116.0	82.9	10.9	1.03

The data found in the literature of the subject to be compared with the present results are that of the compound I 0.79D measured by Freiser, Eagle and Speier[8], which is in good agreement with ours. Sauer and Mead found the values 0.74D and 1.09D for the moment of I and III respectively. Their results, however, should not be compared directly with our results, since their measurements were carried out on pure liquids.

Discussion of the Results

Polarity of Si-O bond If we use $\angle SiOSi = 130°$, evaluated from electron diffraction data of the experiment on I,[9] and the moment of 0.80D observed for I, the moment of Me_3SiO-group can be calculated as $0.80/(2\cos 65°)=0.95D$**, which is identical with the value estimated by Freiser and others. It is only half as great as the value, 2.2D estimated by Sauer and Mead[4]. On the assumption that the bond moment of O-H is equal to 1.5D and the valency angle SiOH to 110°, the moment of trimethylsilanol is calculated to be 1.5D or 2.2D, according to the value of Me_2SiO-group moment of 0.95D or 2.2D. If we compare these values with the observed moment of Et_3SiOH[10], 1.50D, it may be concluded that the Me_3SiO-group moment estimated by us is more proper than that of Sauer and Mead***. Subtracting the bond moment of Si-C (1.0D) and H-C (0.4D) algebraically from the Me_3SiO-moment (0.95D), we obtain the Si-O bond moment as 1.55D.

If we take into consideration the contribution of the ionic structure $Si^+—O^-$ only, the Si-O moment is calculated to be 3.2D, twice as large as the observed value. This discrepancy is explained as follows. It has generally been acknowledged by many authors that silicon has an ability to expand the valency shell beyond octet and to from multiple bonds. Therefore the $Si^-=O^+$ double bond structure contributes to the normal state in such a manner as to cancel the moment of $Si^+—O^-$ structure partly. Pauling[11] presented an elaborate method of calculating the percentage character of the polar and the double bond structure in oxygen acid, such as silicate ion. If we apply his method to the bond of siloxane, the ionic character of $Si^+—O^-$ is estimated to be 41%, the double bond character of $Si^-=O^+$ to be 27% and the Si-O bond length to be 1.63A. From these values, SiO moment is calculated to be 1.1D, which agrees fairly well with the observed value of 1.55D, considering the approximations made in the calculation.

Atomic Polarization of Cyclotrisiloxane and Cyclodithiosiloxane From an electron diffraction study of hexamethylcyclotrisiloxane II, Aggerwal and Bauer[1] concluded that it has a planar structure. Frevel and Hunter[3] reached the same conclusion from an X-ray investigation on it. Accordingly it is reasonable to assume that it has a planar structure with no permanent moment even in

* T. Nomura, M. Yokoi and K. Yamasaki, *Proc. Japan Acad.*, **29**, 342 (1953).

6) Y. Kurita, T. Nozoe and M. Kubo, This Bulletin, **24**. 10 (1951).

7) Y. Kurita, T. Nozoe and M. Kubo, This Bulletin, **26**, 242 (1951).

8) H. Freiser, M. V. Eagle and J. Speier, *J. Am. Chem. Soc.*, **75**, 2824 (1953).

** If we use the value of $\angle SiOSi=137°$ cited in *Ann. Rev. Phys. Chem.*, **2**, 224 (1951) instead of 130°, the moment of Me_2SiO-group is calculated as 1.09D.

*** From the constancy of the moments per monomeric units of dimethylsiloxane polymers greater than tetramers, they concluded that $-O-=160°$ and that the group moment of Me_2SiO is equal to 2.2D. However, the observed moments can be explained adequately with our value for the bond moment, if a slight hindrance of rotation about Si-O bond is assumed to be present.

9) K. Yamasaki, A. Kotera and M. Yokoi, *J. Chem. Phys.*, **18**, 1414 (1950).

10) M. Pizotti, *Gazz. Chim. Ital.*, **73**, 143 (1943).

11) L. Pauling, *J. Phys. Chem.*, **56**, 361 (1952).

solution. Then we are led to the conclusion that II has the atomic polarization of 10.9 cc., amounting to 20% of the electronic polarization. It is not an unreasonable value as compared with the large atomic polarization of compounds with a similar ring structure, such as paraldehyde (11.4 cc.) and trioxane[12] (13 cc.). Baker et al.[13] obtained large atomic polarizations for linear polysiloxanes.

In the molecule IV, the distortion of the valency angle of SiSSi and SSiS and the repulsion between methyl groups across the ring are minimum for the planar configuration. This supposition was confirmed by Yokoi and Nomura[5] with an electron diffraction study. Hence it can be assumed that IV has a planar structure with no permanent dipole moment. Then the atomic polarization is estimated as $P-R_D=9$ cc.

These results will be used later for the estimation of the atomic polarizations of III and V.

Configuration of Octamethylcyclotetrasiloxane If the atomic polarization of III is assumed, from analogy to II, to be 14.5 cc. or 20% or R_D, the moment of III is calculated to be 0.67D. From the electron diffraction study Yokoi[2] determined the valency angles of O and Si and bond lengths, but he failed to draw a definite conclusion concerning the configuration of the molecule. Among the possible symmetrical configurations, only the crown form has a finite moment (1.7D)*, while the cradle and tub forms have no moment. The possible explanation of the observed moment (0.67D) is that III exists either as mixture of these symmetrical forms or as a certain less symmetrical form intermediate between these symmetrical forms. For example, D-form has a moment of 0.6–0.7D.

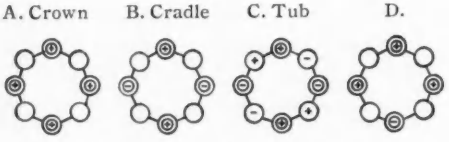

Fig. 1

Configuration of Hexamethylcyclotrithiosiloxane V has a moment of 1.03D, even if it has an atomic polarization 10.9 cc., the same value in magnitude as that of the corresponding oxygen compound II. The large of 1.03D for V rules out the planar symmetrical model similar to that in II.

The theoretical values for the chair and the boat configurations were calculated as follows. The moment of the chair form is given by $\mu=3\sin\theta\mu_{SSiS}$. In this expression, θ, the angle between the SSS plane and the SSiS plane, is calculated from the relation,

$$\cos\theta=(2\sin\alpha/2-\sin\beta/2)(\sqrt{3}\cos\beta/2),$$

where α is the valency angle of SiSSi and β the valency angle of SSiS. Assuming the bond moment of Si-S**, Si-C and H-C to be equal to 1.0D, 1.0D and 0.4D, respectively, and the valency angle of Si to be tetrahedral, the $SSi(Me_2)S$ group moment, μ_{SSiS}, is calculated as 0.62D. On these assumptions, the resultant moment of the chair form is calculated to be 1.06±0.14D for the value of α equal to 110±5°, obtained from the electron diffraction by Yokoi and Nomura[5]. The moment of the boat form is calculated to be equal to about one third of that of the chair form. From the comparison of these values with the observed one, V appears to have predominantly the chair configuration. As the moment of the boat form is relatively smaller than that of the chair form, the existence of a small amount of the former does not affect appreciably the theoretical value of the moment of the mixture. When $\alpha=110°$, a mixture composed of 94% of the chair form and 6% of the boat form gives exactly the observed value, 1.03D. When $\alpha=105°$, the composition is 73%-27%. Hence the apparent agreement between the observed and the calculated moments does not preclude the existence of the boat form definitely. On the other hand, it is expected also from the consideration of the moleular model that the boat form of V is not significantly unstable compared with the chair form since the large Si-S distance will decrease steric repulsions. It is desirable to study the possibility of the existence of the boat form.

Summary

The dipole moments of several cyclosiloxanes and cyclothiosiloxanes were measured in benzene solution. The values obtained are: Hexamethyldisiloxane (I), 0.80D; octamethylcyclotetrasiloxane (III), 0.67D; hexamethylcyclotrithiosiloxane (V),

12) R. J. W. Le Fèvre, J. W. Mully and B. M. Smyth, *J. Chem. Soc.*, **1950**, 230.

13) E. B. Baker, A. J. Barry and M. J. Hunter, *Ind. Eng. Chem.*, **38**, 1117 (1946).

* In obtaining this value, we used the following values ∠SiOSi=140°, ∠OSiO=115° evaluated from electron diffraction study by Yokoi and H-C=0.4D, Si-C=1.0D and Si-O =1.55D estimated above.

** The ionic character of the Si—S bond is estimated to be equal to 11% from the electronegativity difference of Si and S. Then the Si—S moment may be taken as 1.0D, using 2.14 Å as the Si—S distance.

1.03D. The atomic polarizations obtained are: hexamethylcyclotrisiloxane (II), 10.9 cc.; tetramethylcyclodithiosiloxane (IV), 9.0 cc. The unexpectedly small bond moment of Si-O (1.55D) can be explained by the double bond character of the bond. For the configuration of (III) and (V), it is impossible to draw any definite conclusion from the study of the dipole moment alone.

We wish to express our sincere thanks to Prof. M. Kubo for his kind advice and encouragement, and to Mr. M. Yokoi for placing the samples at our disposal and for many stimulating discussions. Our tnanks are also due to the Ministry of Education for a contribution in aid of this research.

Chemical Department, Faculty of Science, Nagoya University, Nagoya

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Molecular Structural Studies on Compounds Containing C—O Bond[1] *by Electron Diffraction. I. Molecular Structure of Gaseous p-Benzoquinone*

By Masao KIMURA and Shuzo SHIBATA

(Received December 25, 1953)

It is well-known that the quantum mechanical treatment can be applied to the problem of the π-electron distribution in a molecule to obtain the relationship between the bond order and bond length[2]. For C-C bond, such treatments have been carried out by many workers and there is much reliable information useful in the discussion of π molecular structure[1], whereas for C-O bond, the relation between the bond order and bond length has not yet been clarified in spite of its interest from the viewpoint of molecular structural theory. This is mainly due to the fact that we lack any abundant informations regarding geometrical configurations. The C-O bond length is affected sensitively by groups or atoms coexistent in the molecule. The difference between the values of the double and the single carbon-oxygen bond distances is larger than that for other heteropolar bonds, e.g. C-N and C-S. The facts mentioned above attract our interests strongly. But we must take into account the state in which the molecular configuration is determined, since the configurations of molecules containing carbonyl, carboxyl and hydroxyl groups are often affected by intermolecular interactions, such as hydrogen bond in crystals[3], in some cases even in the gaseous state. Therefore, it seems to be preferable to determine molecular structures not only by X-ray diffraction but also by gas electron diffraction. Our investigations have been undertaken in order to determine molecular structures in the gaseous state and to discuss the relationship between the bond order and bond length. The structure of methyl and ethyl alcohol[4], 1.4-dioxane[5], trioxane[5] and acetone[5] have already been investigated in our laboratory. It is desirable to choose, as material, molecules, whose physicochemical properties are well-known. The ultraviolet absorption[7] and diamagnetic anisotropy[8] of *p*-benzoquinone suggest that C=O bond is conjugated with another double bond in the molecule. It is also known that *p*-benzoquinone and hydroquinone form a molecular compound, quinhydrone. Therefore these were taken as the materials for our first investigation. The molecular structure of *p*-benzoquinone has already been studied by Robertson[9] with X-ray diffraction by crystal. Though it may be considered that the molecular structure of *p*-benzoquinone in the crystalline state is identical to that in the gaseous state, for the reason mentioned above we believe that it is necessary to determine the molecular structure of gaseous *p*-benzoquinone by the electron diffraction method and to compare the result with the value obtained by X-ray diffraction method. We could not determine the molecular structure of hydroquinone by use of the visual method with sufficient accuracy to discuss the properties of C-O bond. Therefore the result for hydroquinone will

1) Cf. e.g. C.A. Coulson and H.C. Longuet-Higgins, *Proc. Roy. Soc.*, A**193**, 450 (1948).
2) Cf. e. g. C. A. Coulson, *Proc. Roy. Soc.*, A**169**, 413 (1939).
3) M. Kimura and M. Aoki, This Bulletin, **26**, 429 (1953).
4) M. Kimura, *J. Chem. Soc. Japan*, **71**, 18 (1950).
5) M. Kimura and K. Aoki, *J. Chem. Soc. Japan*, **72**, 169 (1951).
6) M. Kimura and Y. Kurita, *J. Chem. Soc. Japan*, **72**, 396 (1951).
7) H. L. McMurry, *J. Chem. Phys.*, **9**, 231 (1941).
8) K. Lonsdale, *Proc. Roy. Soc.*, A**171**, 559 (1939).
9) J. M. Robertson, *Proc. Roy. Soc.*, A**150**, 106 (1935).

be reported after reinvestigation is carried out by the electron diffraction method with a rotating sector.

TABLE I
OBSERVED VALUES OF q FOR p-BENZOQUINONE

Max.	Min.	q	Max.	Min.	q
2		18.41	8		58.17
3		24.70		8	61.48
4		29.73	9		64.25
	4	32.79		9	65.96
5		35.15	10		68.57
	5	38.31		10	71.63
6		41.77	11		74.03
	6	48.27		11	76.64
7		51.96	12		79.80
	7	55.08			

Experimental

p-Benzoquinone was prepared by the oxydation of aniline, and was purified before use: m.p. 116°C. A temperature nozzle[9] was used in order to obtain the vapor of p-benzoquinone. Seven photographs were taken using a camera length of about 11 cm.[10] and an electron wavelength of about 0.06 Å. Measurements were, as usual, carried out by the visual method[11].

The characteristic features of the photograph are shown in curve V of Fig. 2, and q values of maxima and minima are listed in Table I. The observed values of the second and third minima are inaccurate owing to the background. Hence these are not listed in Table I. The radial distribution curve was calculated by the use of the formula

$$rD(r)=\sum_{q=1}^{\max} I(q)\cdot\exp(-aq^2)\ \sin(\pi qr/10)$$

where a was taken as $\exp(-aq^2_{\max})=0.1$. The dotted line in the visual curve was obtained by the use of the theoretical intensity curve for a model obtained from preliminary calculation of the radial distribution curve. The final radial distribution curve is shown in curve R.D. in Fig. 2. The curve has sharp maxima at 1.50 Å, 2.46 Å and 3.55 Å, corresponding to C_1—C_2, C_1—C_3, C_2—C_5 and C_3—O_1 respectively. The shelf at the left side of the peak at 1.50 Å is attributable to C_1—O_1 and C_2—C_3 (cf. Fig. 2). The peaks corresponding to the other interatomic distances could not be distinguished from ghosts since they contribute negligibly to the radial distribution curve. Though the peak at 1.50 Å might be affected slightly by the contribution of shorter interatomic distances represented as a shelf, it may be concluded that C_1—C_2 and C_2—C_3 interatomic distances are definitely different from each other and that C_1—C_2 distance is approximately equal to 1.50 Å.

The simplified theoretical intensity curves

$$I(q)=\sum_i\sum_{i<j}\frac{z_i z_j}{r_{ij}}\sin\ (\pi q r_{ij}/10)$$

were calculated for the values ranging from 106° to 103° for $\angle\alpha$, 1.48 Å to 1.54 Å for r(C—C), 1.28 Å to 1.36 Å for r(C=C), as-

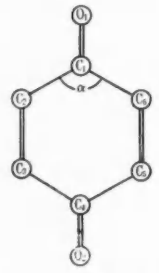

Fig. 1. p-benzoquinone.

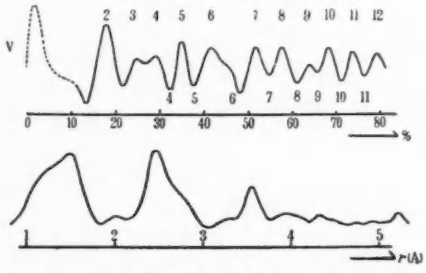

Fig. 2. Visual and radial distribution curves.

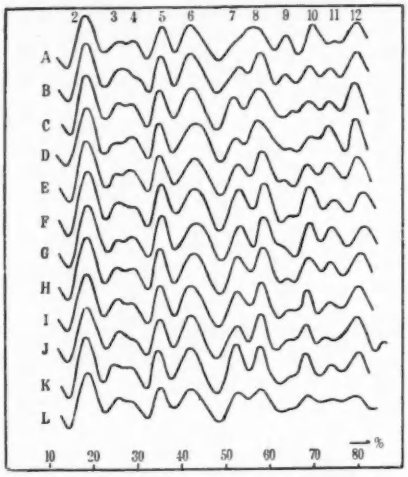

Fig. 3. Theoretical intensity curves for p-benzoquinone.

10) M. Kimura, Chemical Research, Vol. 9, p. 53.
11) Cf. e. g. L. O. Brockway, *Rev. Mod. Phys.*, 8, 231 (1937).

TABLE II
MODELS FOR *p*-BENZOQUINONE

	C=O (A)	C—C (A)	C=C (A)	$\angle\alpha$
A	1.14	1.52	1.32	116
B	1.14	1.52	1.32	112
C	1.14	1.52	1.32	110
D	1.14	1.50	1.34	110
E	1.14	1.50	1.32	110
F	1.14	1.50	1.28	116
G	1.14	1.48	1.30	110
H	1.14	1.50	1.30	110
I	1.14	1.52	1.30	110
J	1.14	1.54	1.30	110
K	1.14	1.52	1.30	108
L	modified I taking the effect of molecular vibrations into account.			

suming that r(C=O) 1.14 Å. A coplanar model was assumed with C—H distance equal to 1.09 Å. With the assumption that r(C=O)=1.14 Å, molecular forms are settled by three parameters, $\angle\alpha$, r(C—C)/r(C=O) and r(C=C)/r(C=O).

Thirty-four theoretical intensity curves were drawn and the relative positions and features of maxima and minima were compared with the visual curve. Some of them are depicted in Fig. 3. The models corresponding to these curves are listed in Table II. With the increasing angle $\angle\alpha$, the positions of the 8th and the following maxima shift to larger q values, and the relative intensity of the 7th and 8th maxima and that of the 9th and 10th maxima change as shown in the curves A, B and C in Fig. 3. r(C=O)/r(C=O) is related mainly to the relative intensities of the 3rd and 4th maxima, of the 7th and 8th maxima and of the 9th and 10th maxima (Curve D, E and F). r(C—C)/r(C=O) is related mainly to the relative intensity of the 9th and 10th maxima (curve G, H, I and J). From the criterion mentioned above, the models F, J and K are chosen as the models in good agreement with the visual curve in qualitative sense. The quantitative comparison with the observed values of maxima and minima was made for the calculated values of the models F, I and K.

The effect of molecular vibrations was taken into account in calculations with the following formula,

$$I(q)=\sum_{i}\sum_{j}^{'}\frac{z_i z_j}{r_{ij}}\exp\left(-b_{ij}q^2\right)\sin\left(\pi q r_{ij}/10\right)$$

in which the values of parameters b_{ij} for carbon-carbon and carbon-oxygen atomic pairs were estimated from the spectroscopic data for benzene and other compounds. In Fig. 3, the curve I is that of the fixed model. When the effect of vibration is taken into account we obtain the curve L. As a result it was shown that the features of intensity curves did not change, except the positions of the maxima farther apart than the 9th one, whose changes were surely within experimental errors.

The following values were obtained for the molecular structure of *p*-benzoquinone: $\angle\alpha=110°\pm2°$, r(C—C)=1.52 Å±0.02 Å, r(C=C)=1.31 Å±0.02 Å, r(C=O)=1.15 Å±0.02Å.

Discussion

Robertson[4] determined the molecular structure of *p*-benzoquinone using X-ray diffraction method. His values are as follows: $\angle\alpha=109°$, r(C−C)=1.50 Å, r(C=C)=1.32 Å, r(C=O)=1.14 Å. These values agree excellently with ours. It follows that intermolecular forces are weak in p-benzoquinone crystal and that a molecule in crystal is in an electronic state similar to a free molecule.

The value of C=O 1.15 Å is very short compared with the normal value of C=O distance in ketotype compounds, such as acetone[5]. The value of C=C distance is nearly equal to a pure double bond distance within experimental errors. In spite of the information of conjugation between C=O and C=C, the result obtained from the diffraction experiments suggests that C=O and C=C double bonds are localized to greater extent. The theoretical discussion in regard to these results will be made in our later paper.

We should like to express our thanks to Prof. M. Kubo for his helpful advice. Our thanks are also due to the Ministry of Education for grants in aid of this research.

Chemical Department, Faculty of Science, Nagoya University, Nagoya

Estrogenic Action of Methylenimine Derivatives

By Yujiro NOMURA

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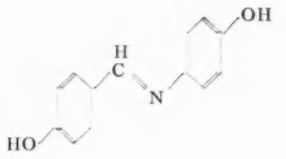
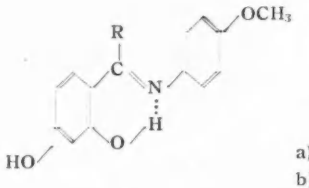
F. W. Schueler suggested that a compound, constituted of a rather large, rigid, relatively inert, and lipoid soluble molecular structure with two active hydrogen-bond forming groups located at an optimum distance of 14.5 Å units from each other may show estrogenic action.[1] He prepared sixteen azomethines and found an example to meet his hypothesis in 4, 4′-dihydroxydiphenylmethylenimine (I), which, administered subcutaneously, produced a true estrogenic response in rats in a total dose of 12.5 mg.[2] However, it must be noted that the activity is rather small for the fulfilment of the requirements.

M. Oki and Y. Urushibara deduced the non-planar structure of stilbestrol and its homologs from their ultraviolet absorption data and presented a hypothesis that in addition to other requirements an optimum thickness of the molecule is an important factor for a strong estrogenic action.[3] The 4, 4′-dihydroxydiphenylmethylenimine prepared by Schueler has a thin structure, and its low activity might be attributed to the lack of the moderate thickness favorable for the development of a high activity.



I



II

R	
a)	CH_3
b)	C_2H_5
c)	$(CH_3)_2CH$

The author prepared alkyl 2,4-dihydroxyphenyl-4′-methoxyphenylmethylenimines (II), which probably have rigid structures by virtue of the chelate ring formation between the nitrogen atom and the ortho-standing phenolic hydrogen atom[4], and at the same time a thickness given by the steric interference of the alkyl substituent with the 4′-methoxyphenylimino group.[5]

The substituted methylenimines were prepared by condensing alkyl 2, 4-dihydroxyphenyl ketone with *p*-anisidine in the presence of anhydrous zinc chloride:

1-$RCOC_6H_3(OH)_2$-2,4+*p*-$NH_2C_6H_4OCH_3$→II

Estrogenic activities were evaluated by the vaginal smear test with ovariectomized mice by subcutaneous injection of oil solutions in two portions. Substance IIa (R: CH_3) was inactive in 1 mg. dosage. The substance IIb (R: C_2H_5) was fully active in 1 mg. dosage, and the substance IIc (R: $(CH_3)_2CH$) produced estrus in 40 % of the animals in the same dosage. The ethyl compound was the most active of the present series as in the stilbestrol homologs. As Schueler pointed out[2], a stronger estrogenic response may be expected when applied by intravaginal injection, because the methylenimine linkage is probably in part cleavaged in vivo before the compound reaches its site of action.

Experimental Part*

Alkyl 2, 4-dihydroxyphenyl Ketone. 1-$RCOC_6H_3(OH)_2$-2, 4.—Prepared according to Org. Syn. Vol. XXI, p. 103 (1941). 55 g. of resorcinol yielded 49 g. of methyl 2, 4-dihydroxyphenyl ketone melting at 142.3–144.3°C, and 48.5 g. of ethyl 2, 4-dihydroxyphenyl ketone melting at 98.2–99.2°C., respectively. 16 g. of resorcinol yielded 8.5 g. of isopropyl 2, 4-dihydroxyphenyl ketone bioling at 164°C./5 mm.

Methyl-2,4-dihydroxyphenyl-4′-methoxyphenyl-methylenimine (II a) 5 g. of methyl 2, 4-dihydroxyphenyl ketone and 6 g. of *p*-anisidine were mixed in a 20 cc. flask and 0.1 g. of anhydrous zinc chloride was added. The flask was immersed in an oil bath and heated at 140°C. for five minutes in a stream of carbon dioxide. The reaction mixture was cooled to the room tempera-

1) F. W. Schueler, *Science*, **107**, 94 (1948).
2) F. W. Schueler, *J. Amer. Pharm. Assoc.*, **39**, 87 (1950).
3) M. Oki and Y. Urushibara, This Bulletin, **25**, 109 (1952).
4) Cf. Y. Urushibara and T. Takahashi, This Bulletin, **26**, 162 (1953).
5) Cf. Reference 3.

* Melting points of methylenimines were determined in sealed capillaries, and corrected.

ture and digested with methanol. Recrystallization from acetone gave yellow plates melting at 262°C. with decomposition (Yield 8.2 g.). Found: C, 70.26; H, 5.80; N, 5.43. Calculated for $C_{15}H_{15}O_3N$ (II a): C, 70.02; H, 5.88; N, 5.44 %.

Ethyl- and isopropyl-2, 4-dihydroxyphenyl-4'-methoxyphenyl-methylenimine (IIb and IIc) Synthesized in the same way as the methyl compound. 5 g. of ethyl 2,4-dihydroxyphenyl ketone and 6 g. of *p*-anisidine yielded 6 g. of ethyl-2, 4-dihydroxyphenyl-4'-methoxyphenyl-methylenimine. Recrystallization from acetone gave yellow leaflets melting at 213°C. with decomposition. Found: C, 71.07; H, 6.07; N, 5.21. Calculated for $C_{15}H_{17}O_3N$ (II b): C, 70.83; H, 6.32; N, 5.16 %.

7.26 g. of isopropyl 2, 4-dihydroxyphenyl ketone and 7.06 g. of *p*-anisidine yielded 4 g. of isopropyl-2, 4-dihydroxyphenyl- 4'-methoxyphenyl-methylenimine. Recrystallization from methanol gave pale yellow crystals melting at 197°C. with decomposition. Found: C, 71.42; H, 6.88; N, 4.82. Calculated for $C_{17}H_{19}O_3N$ (II c): C, 71.56; H, 6.71; N, 4.91 %.

These methylenimine derivatives were readily hydrolyzed by diluted hydrochloric acid to *p*-anisidine and corresponding alkyl 2, 4-dihydroxyphenyl ketone.

The author wishes to express his hearty thanks to Professor Y. Urushibara for his kind guidance and encouragement. Thanks are also due to Mr. F. Ueno, Teikoku Hormone Manufacturing Co., Ltd., Kawasaki, for the bio-assays and to the Ministry of Education for the Grant in Aid for Fundamental Scientific Research.

Chemical Institute, College of General Education, Tokyo University, Tokyo

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*A Nitrogen Analog of Hexestrol, Ethyl-p-hydroxyphenyl-(1-p-hydroxyphenyl-propyl)-amine, and Its Derivatives**

By Yujiro NOMURA

(Received January 11, 1954)

Various oxygen and sulfur analogs of hexestrol have been prepared and found to have estrogenic activities.[1] These facts show that the member constituting the molecular skeleton of hexestrol may be replaced by a different atom without destroying totally the estrogenic activity, unless a significant change in the molecular shape and the appearance of any new physiological properties are associated with the introduction of the different atom.

The author prepared a nitrogen analog of hexestrol, ethyl-*p*-hydroxyphenyl-(1-*p*-hydroxyphenyl-propyl)-amine, *p*-$HOC_6H_4N(C_2H_5)CH(C_2H_5)C_6H_4OH$-*p*, as follows: Dry hydrogen bromide was passed into an ethereal solution of anethole (3.11 g.), and the resulting solution of the addition product was mixed with a pyridine solution containing an equivalent amount of ethyl-*p*-methoxyphenyl-amine, prepared according to King and Tonkin.[2] After standing overnight the reaction mixture was shaken with water. From the upper layer ethyl-*p*-methoxyphenyl-(1-*p*-methoxyphenyl-propyl)-amine (3.39 g.) was isolated and recrystallization from methanol gave colorless prisms, melting at 64.5–65.0°C. Found: C, 76.20; H, 8.50; N, 4.70. Calculated for $C_{19}H_{25}O_2N$: C, 76.22; H, 8.42; N, 4.68%.

This amine developed incomplete but distinct durable estrus in the dosage of 60 γ by subcutaneous injection into ovariectomized mice in two portions in oil solution as referred to elsewhere.[3]

Ethyl-*p*-hydroxyphenyl-(1-*p*-hydroxyphenyl-propyl)-amine was obtained by the demethylation of the above substance with red phosphorus and hydroiodic acid (d=1.7) in colorless crystals melting at 100.5°C. after recrystallization from benzene. Found: C, 75.32; H, 7.61; N, 5.30. Calculated for $C_{17}H_{21}O_2N$: C, 75.24; H, 7.80; N, 5.16%.

Acetylation of ethyl-*p*-hydroxyphenyl-(1-*p*-hydroxyphenyl-propyl)-amine with acetic anhydride gave a diacetate melting at 54–55°C. Found: N, 3.61. Calculated for $C_{21}H_{25}O_4N$: N, 3.94%.

The author wishes to express his hearty thanks to Professor Y. Urushibara for his kind guidance and encouragement. Thanks are also due to Mr. F. Ueno, Teikoku Hormone Manufacturing Co., Ltd., Kawasaki, for the bio-assays and to the Ministry of Education for the Grant in Aid for Fundamental Scientific Research.

Chemical Institute, College of General Education Tokyo University, Tokyo

* All melting points are corrected.

1) Y. Urushibara and M. Oki, This Bulletin, **23**, 35 (1950). Y. Urushibara and T. Takahashi, ibid, **23**, 53 (1950), Y.Urushibara and M. Oki and R. Ikeda, ibid, **25**, 66 (1952).

2) Harold King and Isabel M. Tonkin, *J. Chem. Soc.*, **1946**, 1063.

3) Y. Urushibara and T. Takahashi, This Bulletin, **23**, 54 (1950).

On Derivatives of α-Thujaplicin. III.[1] *Azo Dyes of α-Thujaplicin (o Isopropyl tropolone)*[2]

By Kameji YAMANE

(Received December 16, 1954)

T. Nozoe and his coworkers[3,4,5] carried out the detailed study about the azo dyes of hinokitiol (*m*-isopropyltropolone) but only *p*-tolyl-azo-dye of α-thujaplicin was reported.[6,7]

Fourteen kinds of azo dyes of α-thujaplicin are described in this paper. The alkali salt of α-thujaplicin was coupled with diazonium salts of aromatic amines in cold aqueous solution to yield orange yellow to reddish brown azo dyes easily and in good yield. The application of an excess diazonium salt gave only a mono-azo compound. The azo dyes obtained are given in Table I.

TABLE I

AZO DYES OF α-THUJAPLICIN OBTAINED

Aromatic amines used.	Color and form	m.p.	Solvents (for recrystallization)
Aniline	red prisms	132.8–134°	alcohol
o-Toluidine	red prisms	120–121°	cyclohexane
p-Toluidine	orange red prisms	130–131°	benzene
p-Anisidine	orange fine needles	107–108°	alcohol
p-Chloroaniline	yellowish brown fine crystal	123–124°	cyclohexane
p-Bromoaniline	reddish brown needles	123–124°	alcohol
m-Nitroaniline	reddish brown fine crystal	144–145.3°	benzene
p-Nitroaniline	reddish brown fine crystal	166–167°	benzene
Sulfanilic acid	orange brown fine crystal	275°<(dec.)	water
p-Sulfanilamide	yellow fine needles	227–228°	acetic acid
p-Aminobenzoic acid	yellow fine crystal	267–268° (dec.)	water (K-salt)
α-Naphthylamine	brownish red plates	135–136°	acetic acid
β-Naphthylamine	red prisms	136–137°	pet.-ether
Benzidine	dark brown fine crystal	249–250° (dec.)	benzene

Most of the azo dyes are soluble in benzene, alcohol, petroleum ether, cyclohexane and glacial acetic acid, but some derived from sulfanilic acid, *p*-sulfanilamide and *p*-aminobenzoic acid are slightly soluble in these solvents. The azo dyes dissolve in a caustic alkali solution to give an orange red or deep red solution, and precipitate with acid. The azo dyes show a red coloration by ferric chloride, characteristic to tropolone nucleus.

p-Tolyl-azo-α-thujaplicin absorbed two molar equivalents of hydrogen when hydrogenated in ethyl acetate with Adams' PtO_2 catalyst, giving amino-α-thujaplicin m.p. 172–173° and *p*-toluidine. Methylation of *p*-anisyl-azo-α-thujaplicin with diazomethane in ether gave *p*-anisyl-azo-α-thujaplicin methyl-ether m.p.

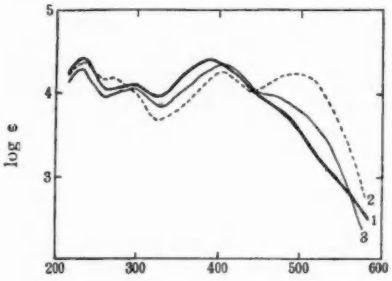


Fig. 1. Ultraviolet absorption spectra of phenyl-azo-α-thujaplicin (Curve 1), *m*-nitro-phenyl-azo-α-thujaplicin (Curve 2), *p*-sulfo-phenyl-azo-α-thujaplicin (Curve 3).

1) H. K. Yamane and S. Morosawa, This Bulletin, **27**, 18, (1954).

2) This work was presented at the Hiroshima District Meeting of the Chemical Society of Japan, Nov. 15 (1953).

3) T. Nozoe, E. Sebe and S. Ebine, *Proc. Japan. Acad.*, **26**, (8) 24 (1950).

4) T. Nozoe, S. Ebine, S. Ito and I. Takasu, Ibid., **27**, 197 (1951).

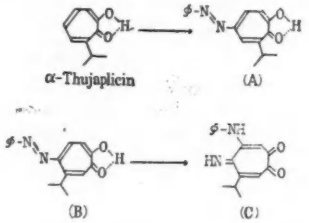
5) T. Nozoe, E. Sebe, Y. Kitahara and H. Fujii, *Sci. Rep. of Tohoku Univ.*, Ser. I., **36**, 166 (1952).

6) T. Nozoe, A. Yasue and K. Yamane, *Proc. Japan Acad.*, **27**, 15 (1951).

7) T. Nozoe, Y. Kitahara, K. Yamane and T. Ikemi, Ibid., **27**, 193 (1951).

99–100°. Ultraviolet absorption spectra of some azo dyes are given in Fig. 1. Absorption maximum of about 400 mμ is characteristic to tropolone nucleus.

T. Nozoe et al.[4,5] have reported that the azo dyes of hinokitiol (B) rearranged when heated with alcohol or acetic acid containing one drop of hydrochloric acid, giving dark reddish purple crystals, that is "hinopurpurins", which have a tropoquinonoid structure (C). It is interesting, however, that all the azo dyes of α-thujaplicin do not undergo rearrangement by the same procedure.



T. Nozoe and E. Sebe[5] have reported that the position of the azo group in azohinokitiols was at the para (5) position in spite of steric interference of the isopropyl group. In the case of azo-α-thujaplicin, the position of the azo group must be either at the para (5) or the ortho (7) position of the cycloheptatrienolone ring.

Amino-α-thujaplicin m. p. 172–173° obtained by the catalytic reduction of *p*-tolyl-azo-α-thujaplicin as described above, is the same substance prepared from the catalytic reduction of nitroso-α-thujaplicin[7] and mononitro-α-thujaplicin m. p. 112–113°.[1]

T. Nozoe et al.[8] have reported that the electrophilic substitution takes place predominantly at the *p*-position in the nitration and the nitrosation of tropolones. From these facts, therefore, the azo coupling of α-thujaplicin may take place at the *p*-position as in (A).

A trial to obtain azoxy-compound by the oxidation of phenyl-azo-α-thujaplicin with 30 per cent hydrogen peroxide solution in glacial acetic acid failed, yielding a syrupy matter which gave no red coloration with ferric chloride.

Beside the crystals of m. p. 131° of *p*-tolyl-azo-α-thujaplicin, the author obtained yellow prisms of m. p. 124° in small amount, but no detailed study has yet been made.

8) (a) T. Nozoe, *Science of Drugs*, **3**, 174 (1949); *Sci. Rep. of Tohoku Univ.*, I, **34**, 199 (1950). (b) T. Nozoe et al., *Proc. Japan. Acad.*, **26**, 33 (1950). (c) T. Nozoe et al, Ibid., **27**, 190 (1950). (d) T. Nozoe and E. Sebe, Ibid., **26**, 45 (1950). (e) T. Nozoe et al., Ibid., **27**, 565 (1951). (f) T. Nozoe et al., Ibid., **28**, 488 (1952).

Experimental

Phenyl-azo-α-thujaplicin [(A)*: $\phi = C_6H_5$-]:—To a solution of 0.11 g. aniline dissolved in 3.3 cc. of 0.93 N-hydrochloric acid, a solution of 0.1 g. of sodium nitrite in 1.5 cc. of water was dropped in, and the resultant cold diazonium solution was added dropwise to the cold solution of 0.2 g. of α-thujaplicin in a mixture of 1.5 cc. of 1.7 N-potassium hydroxide solution and 15 cc. of water. After the completion of the addition, the mixture was stirred for ten minutes and 1 cc. of 2 N-hydrochloric acid was added. The mixture was stirred for a further 30 minutes in the cold, and the crystals were collected by filtration. 0.34 g. of azo dye was obtained. The recrystallization from alcohol yielded red prisms, m. p. 133–134°. Found: C, 71.32; H, 5.87; N, 10.39, Calculated for $C_{16}H_{16}O_2N_2$: C, 71.62; H, 6.01; N, 10.44%.

Azo-α-thujaplicins derived from *o*- and *p*-toluidine, *p*-anisidine, *p*-chloroaniline, *p*-bromoaniline, *m*- and *p*-nitroaniline, sulfanilic acid, *p*-sulfanilamide, *p*-aminobenzoic acid, α- and β-naphthylamine and benzidine were prepared in a manner like the above (ordinary method). The color, crystalline form and melting point of these azo dyes are shown in Table I. [(A): $\phi = o\text{-}CH_3\cdot C_6H_4$-]. Found: N, 10.04, Calculated for $C_{17}H_{18}O_2N_2$: N, 9.92%. [(A): $\phi = p\text{-}CH_3\cdot C_6H_4$-]. Found: N, 9.39, Calculated for $C_{17}H_{18}O_2N_2$: N, 9.92%. [(A): $\phi = p\text{-}CH_3O\cdot C_6H_4$-]. Found: N, 9.16, Calculated for $C_{17}H_{18}O_3N_2$: N, 9.39%. [(A): $\phi = p\text{-}Cl\cdot C_6H_4$-]. Found: N, 9.20, Calculated for $C_{16}H_{15}O_2N_2Cl$: N, 9.25%. [(A): $\phi = p\text{-}Br\cdot C_6H_4$-]. Found: N, 7.99, Calculated for $C_{16}H_{15}O_2N_2Br$: N, 8.07%. [(A): $\phi = m\text{-}NO_2\cdot C_6H_4$-]. Found: N, 13.63, Calculated for $C_{16}H_{15}O_4N_3$: N, 13.41%. [(A): $\phi = p\text{-}NO_2\cdot C_6H_4$-]. Found: N, 13.63, Calculated for $C_{16}H_{15}O_4N_3$: N, 13.41%. [(A): $\phi = p\text{-}HO_3S\cdot C_6H_4$-]. Found: N, 7.87, Calculated for $C_{16}H_{16}O_5N_2S$: N, 8.04%. [(A): $\phi = p\text{-}H_2NO_2S\cdot C_6H_4$-]. Found: N, 12.20, Calculated for $C_{16}H_{17}O_4N_2S$: N, 12.09%. [(A): $\phi = p\text{-}HOOC\cdot C_6H_4$-]. Found: N, 9.04, Calculated $C_{17}H_{16}O_4N_2$: N, 8.97%. [(A): $\phi = \alpha\text{-}C_{10}H_9$-]. Found: N, 8.82, Calculated for $C_{20}H_{18}O_2N_2$: N, 8.80%. [(A): $\phi = \beta\text{-}C_{10}H_9$-]. Found: N, 8.32, Calculated for $C_{20}H_{18}O_2N_2$: N, 8.80%. *p, p'*-Diphenyl-bisazo-α-thujaplicin: Found: N, 10.60, Calculated for $C_{32}H_{30}O_4N_4$: N, 10.48%.

Catalytic reduction of *p*-tolyl-azo-α-thujaplicin:—A solution of 5.22 g. of *p*-tolyl-azo-α-thujaplicin in 150 cc. of ethyl acetate was catalytically reduced with 0.21 g. Adams' PtO_2 at ordinary temperature and pressure, by which 1050 cc. of hydrogen was absorbed. The removal of the solvent and the catalyst gave a solid residue, crude amino-α-thujaplicin. The recrystallization from benzene yielded yellow prisms m. p. 172–173°. Found: C, 67.20; H, 7.26; N, 7.59, Calculated for $C_{10}H_{12}O_2N$: C, 67.04; H, 7.26; N, 7.80%.

The author wishes to express his sincere thanks to Prof. A. Yokoo for his kind guidance, also to Prof. T. Nozoe (Tohoku Univ.) for helping him with this work. The author

* Formula of azo-dyes of α-thujaplicin

thanks also Miss K. Kato and Miss Iwanaga (Nozoe Laboratory) for carrying out the measurements of ultraviolet absorption spectra, and also Mr. Furukawa (Sankyo Co.) and Miss H. Iwata (Kyoto Univ.) for carrying out the microchemical analysis.

Department of Chemistry, Faculty of Science, Okayama University, Okayama, Japan

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Molecular Structure Investigations by Electron Diffraction Method. I. The Molecular Structures of Isopropyl Alcohol and -Chloride

By Mashio YAMAHA

(Received January 19, 1954)

Previous electron diffraction investigations of substituted paraffines, having the number of carbon atoms up to C_3 or C_4, gave various kinds of information about the structures of respective molecules, that is, reliable molecular parameters including the informations about the internal rotations in some kinds of molecules were obtained. In Table I, there are shown several data obtained recently by many authors. Nowadays, the investigations have been carried out using the visual method and also more quantitatively by the use of the apparatus having a sector.

TABLE I

THE LIST OF MOLECULAR CONSTANTS OF SEVERAL PARAFFINE DERIVATIVES FROM RECENT INVESTIGATIONS

Molecules	C-C (Å)	C-X (Å)	Other parameters	References
CH_3–CH_3	(C–H/C–C=1.115/1.54)		∠CCH=110.5°	(6)
CH_3–CH_2OH	1.54	C–O=1.48±0.04		(7)
CH_2Cl–CH_2OH	1.54	C–O=1.45 (1.43)	(Gauche form is predominant at room temperature.)	(8), (9)
CH_2Cl–CH_2Cl	1.49±0.03	C–Cl=1.78±0.01 C′···Cl=2.69±0.02,	(Gauche=27±5% at 22°C.)	(10)
CH_3–CCl_3	1.54±0.04	C–Cl=1.77$_5$±0.02		(11), (12), (13)
CH_3–CCl_2–CH_3	1.54±0.04	C–Cl=1.77$_6$±0.02,	∠ClCCl=109.5±2° ∠CCCl=109°±3°	(11)
CH_2Cl–$CHCl$–CH_3	1.56	C–Cl=1.79±0.035 C′···Cl=2.715±0.025,	∠CCCl=108±4°	(14)
CH_3–CF_3*	1.52±0.02	C–F=1.37±0.02		(15)
CF_3–CF_3*	1.45(±0.06)			(16)

*Origin of the deviations of molecular parameters seem to be somewhat different for fluorinated derivatives from that for other substituted paraffines.

There seem to be disagreements on several points of molecular parameters among a few examples shown in Table I. But whether these discrepancies are within a range of errors or whether they indicate real differences among the molecules could not be decided at present. As regards the C—C bond distances, for example, the value 1.54 Å has so far been usually considered to be reliable for saturated paraffines and their derivatives, but the value 1.49 Å has been obtained for 1,2-dichloroethane molecule[10], and 1.56 Å for 1,2-dichloropropane molecule[14]. The present author is trying to investigate some substituted paraffines as regards the C—C distances and other molecular parameters.

Isopropyl alcohol and -chloride molecules have been investigated, because the contribution of C—C atom-pairs to the intensity curves seems to predominate in these molecules over the cases of ethane derivatives. In this study, we may not ignore the question how the equilibrium positions of two methyl groups will contribute to the intensity

curves. But in the reinvestigation of isopropyl chloride molecule[1], unfortunately, the problem of internal rotations of methyl groups has not been made clear by using the visual method.

Experimental Procedures

Commercial isopropyl alcohol was carefully dried on quick lime and distilled several times (boiling point: 82 °C). The chloride was synthesized[2] from purified alcohol and distilled carefully (b.p. 37°C).

The apparatus of electron diffraction is the one which was described in the previous report[3]. Eight maxima and five minima have been observed visually in the range $9<q<80$ for isopropyl alcohol, and twelve maxima and eight minima in the range $9<q<95$ for isopropyl chloride from ten or more photographic plates in both cases.

The experimental visual curve obtained for each case is shown in the top-most place of Fig. 3A and 3B respectively, and $q_{o's}$'s, the corresponding observed q-values of maxima and minima, are shown in the third column in Table IV A and IV B.

The theoretical intensity curves for the assumed molecular models have been calculated by the use of the well-known formula[4]:

$$I=k\sum_i\sum_j Z_iZ_j/l_{ij}\cdot\left(\sin\frac{\pi}{10}ql_{ij}\right)\cdot\exp(-b'_{ij}q^2)$$

where $q=10\,s/\pi$, $s=(4\pi\sin\theta/2)/\lambda$, θ the scattering angle, and λ the wave length of the beam.

In constructing the assumed molecular models, the rotations of methyl groups about each C–C bond are considered. (The figures of molecular models are shown in Fig. 1, in which various parameters are given out.) That is, all the hydrogen atoms of methyl groups, which contribute to intensity curves as the variations of C″···H and X″···H* distances, are taken into account**.

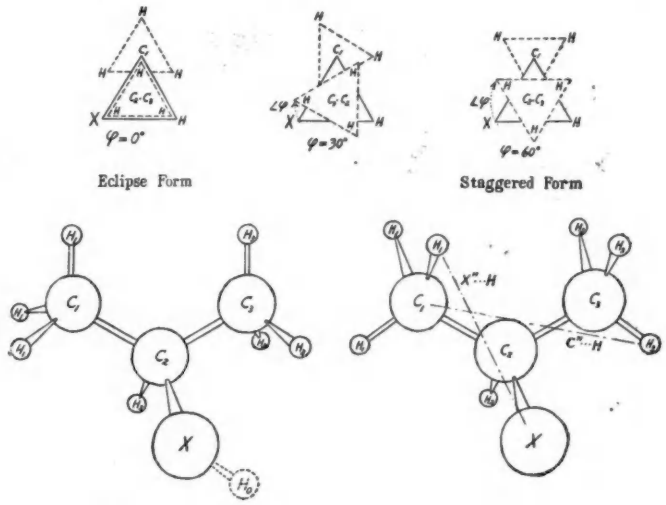


Fig. 1. Schematic models which show the interatomic configurations in relation to the rotations of methyl groups for isopropyl derivatives.

In case of isopropyl alcohol, the atom X is the hydroxyl oxygen and the hydroxyl hydrogen atom H_0 attached to the X atom, which are shown with dotted figure. In case of isopropyl chloride, X is the chlorine atom. One of the six $C''\cdots H$ and one of the six $X''\cdots H$ interatomic distances are hereby exemplified, and the meaning of the signs (″) and (···) will be clear from this figure.

1) J. Y. Beach and D. P. Stevenson, *J. Am. Chem. Soc.*, **61**, 2643 (1939).
2) "Organic Synthesis" Collective Vol. 1, p. 142 (1948), (Analogous method for *n*-Butyl Chloride.)
3) T. Yuzawa and M. Yamaha, This Bulletin, **23**, (No. 8) 414 (1953).
4) V. Schomaker and R. Spurr, *J. Am. Chem. Soc.*, **64**, 2693 (1942).

* The sign (...) shows the distance between two atoms which are non-bonded. The sign (″) shows that there are two other atoms in between along three successive bonds (assigned the mark of *two* dashes), e.g. C″...H shows one of the three $C_1''\ldots H_3$ distances in the case of C_1-C_2-C_3-H_3 as well as $C_3''\ldots H_1$ in C_3-C_2-C_1-H_1.

** The hydrogen atom H0 attached to the oxygen atom of hydroxyl group is neglected, because the contributions of O-H0, $C_2''\ldots H_0$ and those of farther distances between H0 and other atoms to the intensity curves are negligibly small.

The variations of these distances in relation to the rotational angle φ of methyl group (the angle φ is conveniently taken from the C_1C_2X plane for $(methyl)_1$ group) are shown

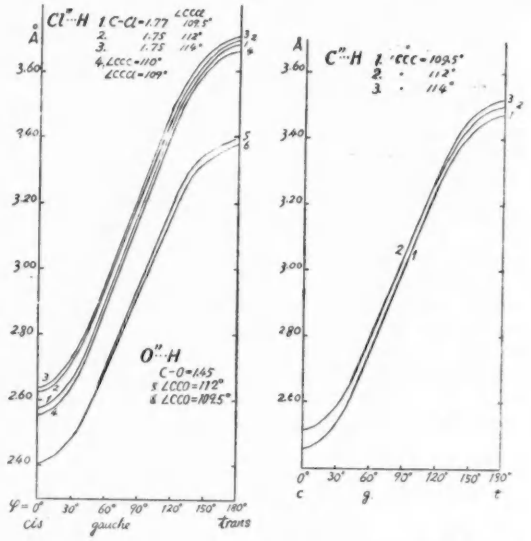


Fig. 2. The diagrams of interatomic distances C''...H, O''...H and Cl''...H versus the rotational angle φ. (In case of C—H=1.10)
Angle φ=0°, 60° and 180° correspond to cis, gauche and trans position respectively about the C—C bond.

in Fig. 2 for each molecule. The contributions of these distances to the intensity curves are remarkable for the alcohol in the range $25<q<55$, where the influences of the thermal vibrations are comparatively small. For the chloride, on the contrary, these contributions appear in the range $q<35$ of the curve, where the exact estimation of the intensity relations is difficult.

The vibration factors b'_{ij} used in the formula are shown in Table II. For isopropyl

TABLE II
THE LIST OF THE APPROXIMATE VIBRATION FACTORS USED FOR THE CALCULATION OF INTENSITY CURVES

Atom pairs	nz_iz_j/l_{ij}**	Distances (Å)	$<l_{ij}^2>_{Av}^{1/2}$	$b_{ij}=\pi/200<1^2_{ij}>_{Av.}$	b'_{ij}
C —C	46	1.52—1.56	0.057	0.00015	0
C'...C	14	2.48—2.55	0.084	0.00035	0.00020
C —H	46	1.09—1.13	0.078 (0.064)*	0.00030	0.00015
C'...H	27	2.14—2.23	0.091 (0.086)*	0.00041	0.00025
C —Cl	58	1.75—1.80	0.061 (0.064)*	0.00018	0.00003
C'...Cl	75	2.68—2.75	0.068 (0.070)*	0.00023	0.00008
C —O	33	1.43—1.48	0.055+	0.00015	0
C'...O	39	2.42—2.46	0.066+	0.00022	0.00008
C''—H (cis, gauche) 6, 11					(0.00060)***
C''—H (120°, trans) 9, 4					(0.00040)***
Cl''...H (cis, gauche) 15, 28					(0.00076)***
Cl''...H (120°, trans) 24, 11					(0.00046)***
C''...H (cis, gauche) 8, 14					(0.00060)***
C''...H (120°, trans) 11, 6					(0.00040)***

Table II. *Reference (10)
**The values are to be some what changed from these values.
***Roughly assumed values.
+Calculated with consideration of reference (5).

alcohol, the values have been assumed by the force constants calculated from vibration frequencies of ethyl alcohol[9]. For isopropyl chloride, the values have been assumed from the values suggested by J. Karle et al.[10].

(The valency agles ∠CCH and ∠HCH are assumed to be 109.5° throughout the investigation.)

Isopropyl Alcohol With the visual curve, the theoretical intensity curves are shown in Fig. 3A in accordance with the variations of assumed molecular models. As shown in Table III A, corresponding theoretical intensity curves to molecular constants of models

TABLE IIIA

THE LIST OF MOLECULAR MODELS AND CORRESPONDING ASSUMED MOLECULAR CONSTANTS FOR ISOPROPYL ALCOHOL

Models	C—C (Å)	C—O (Å)	∠CCC°	Configulation of two $-CH_3$ groups	$q/q_{obs.}$
A	1.54	1.48	109.5	Eclipse	0.991_5
B_E	〃	1.45	〃	〃	1.000_2
C	〃	1.43	〃	〃	1.002_0
D	〃	1.48	112	〃	—
E	〃	1.45	〃	〃	0.995_1
F	〃	1.43	〃	〃	—
B_{30}	〃	1.45	109.5	$\varphi=30$	0.991_9
B_S	〃	〃	〃	Staggered	0.998_7*
P_E	1.52	1.45	109.5	Eclipse	1.012_5
P_S	〃	〃	〃	Staggered	1.006_4*
Q_E	1.56	〃	〃	Eclipse	0.990_7
Q_S	〃	〃	〃	Staggered	0.987_2*
X_E	1.54	1.45	109.5	Eclipse	0.997_5 (C-H=1.13 Å)
Y_S	〃	〃	112	Staggered	— (∠CCO=112°)
Y_{30}	〃	〃	〃	$\varphi=30$	— (〃)

* The 3rd and 5th maxima are not taken into account in these mean values.

TABLE IVA

OBSERVED q-VALUES AND CALCULATED $q/q_{obs.}$ VALUES FOR BETTER MOLECULAR MODELS OF ISOPROPYL ALCOHOL

Max.	Min.	$q_{obs.}$	wt.	A	B_E	B_{30}	C	E	X_E	B_S
	2	(14.39)								
2		18.43	1	1.010	1.023	1.004	1.028	1.010	1.031	0.982
	3	23.13	2	0.997	1.003	0.999	1.002	0.990	1.007	0.994
3		27.20	2	0.995	1.004	1.011	1.007	1.002	1.007	—*
	shelf									
	4	(38.61)								
4		42.59	2	0.991	1.003	0.996	1.003	0.993	0.998	0.996
	5	48.21	2	0.991	1.000	0.975	0.998	0.994	0.994	(1.008)
5		52.36	1	0.974	0.980	0.951	0.985	0.976	0.974	—*
6		58.33	2	0.991	0.998	0.996	1.001	1.000	0.989	1.006
	7	63.79	1	0.979	0.992	0.991	0.992	—	0.986	0.995
7		68.33	1	—	0.995	0.988	—	—	0.985	0.995
8		(76.23)	(See Fig. 3A.)							
Weighted mean:				0.991_5	1.000_2	0.991_9	1.002_0	0.995_1	0.997_6	0.998_3
Wtd. mean sq. deviation:				0.008_3	0.008_2	0.015_0	1.008_7	0.008_8	—	—

*These values can not be taken into account since the features are different from that of visual one. (See Fig. 3A).

are specified as follows:

1) For the groups of curves from A to C and D to F, the C–O distance increase successively in each group. The angles ∠CCC are 109.5°, 112° in the two groups respectively and other parameters, ∠CCO and rotational configurations, remain constant.

2) Curves assigned P, B, Q in order correspond to the increase of C–C distance with constant other parameters.

The $q_{obs.}$'s of the maxima and the minima

(abbreviated as "*q-values*" in this and next sections) of each curve in the cases 1) and 2), are slightly different from one another with the parameters mentioned, and the curves assigned B, including the subscripts, seem to be the most acceptable ones.

3) Curves assigned the same letters with different subscripts (e. g. B_E, B_{30}, B_S; P_E, P_S; Q_E, Q_S; and Y_E, Y_S) show the different rotational configurations of methyl groups with the same other parameters in each case, i. e. "E", "30" and "S" show the cases in which the angles φ are 0°, 30° and 60° respectively.

Through each group, for example B_E, B_{30} and B_S, the remarkable variations of the curves are shown by the features of the third maximum with the shelf-like maximum and the fifth maximum. The curves with subscripts "S" are at least to be rejected through these groups, and curves B_E and B_{30} are the acceptable ones. This selection seems to be confirmed, although the visual method used.+

4) The curves X_E and X_S, correspond to the case of C–H=1.13 Å, and have shown slight disagreements in *q-values*. The curves Y correspond to the model having the both angles $\angle CCC = \angle CCO = 112°$, and are to be rejected because the *q-values* and the shapes of the fifth minimum and the fifth maximum are different obviously from the visual one.

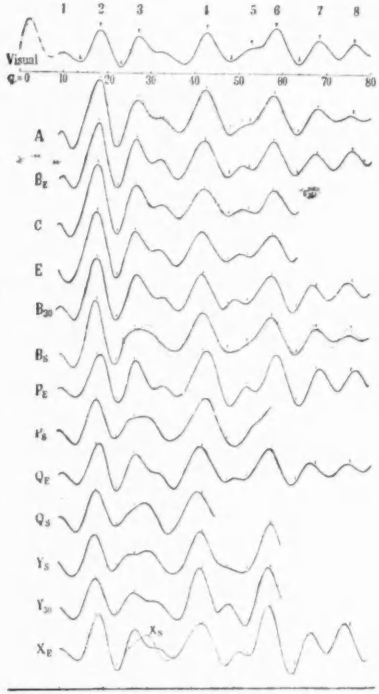


Fig. 3 A. Visual and theoretical intensity curves for isopropyl alcohol molecule.

Dotted curves on *A* and *Bs* correspond to the curves of each rigid model, and real curves *A* and *Bs* to the curves in which the vibration factors for each atomic distance as shown in Table II are taken into account. (In the other real curves, the factors are not taken into account for convenience, because the effects of the factors are not large enough to change the features of each maximum and minimum.)

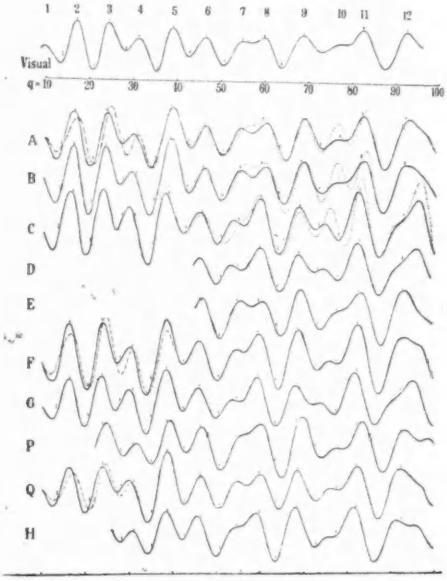


Fig. 3B. Visual and theoretical intensity curves for isopropyl chloride molecule.

Broken curves on A, F and Q in the range of $q<45$ correspond to each eclipse model, and all real curves in this q-range to each staggered model. Dotted curves on A, B and C in the range of $q>40$ correspond to the curves of each rigid model, and in all real curves from A to R in this q-range, the vibration factors are taken into account. The damping effects to the features of the curves seem to be remarkable in the range of $q>50$, especially the tenth maximum and the eleventh minimum.

+ In order to obtain the better visual curve, especially to confirm the intensity relation of the third maximum with the following shelf and the fifth small maximum, we have photographed by the use of a new apparatus, which has 1 s^2 sector and the camera length about 11.82 cm., which has recently been constructed and is now in regulating. But since the microphotometry could not yet be applied, we have measured carefully by the visual method.

The influence of the vibration factors using the values above mentioned are shown with the dotted curves on the curves A and Bs.

The radial distribution curve was computed using the best visual intensity curve (see Fig. 4), The background line is almost smoothed out and the each peak of the

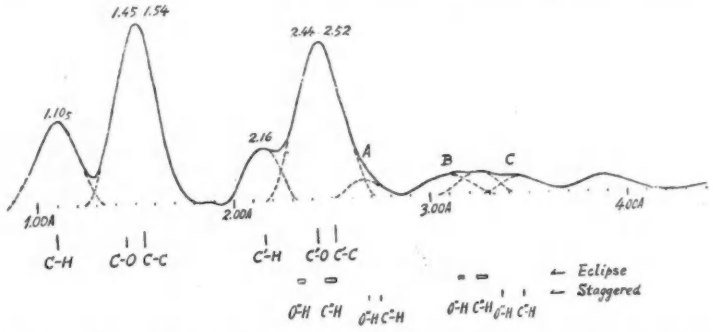


Fig. 4. Radial distribution curve for isopropyl alcohol molecule computed using the visual curve.

Under the curve, the interatomic distance corresponding to each peak is shown, and O''...H and C''...H distances are pointed out at lower levels. Interatomic distances, O''...H and C''...H, are to correspond to either level, (eclipse or staggered), in accordance with the variation of the rotational configurations. But the figures indicated by A, B and C are somewhat obscure.

curve seems to correspond almost correctly to each distance of all atom-pairs of the best model. The combinations of atomic distances O'' . . . H and C'' . . . H, corresponding to both the eclipse and staggered form of methyl groups seem to appear. From the feature of this curve, however, the fact can not be decided whether these might be the ghost maxima or not (marked with A, B and C in Fig. 4).

Isopropyl Chloride.—The visual curve and theoretical intensity curves are shown in Fig. 3B. Molecular parameters used in obtaining each theoretical curve are listed in Table IIIB. The characteristic features of the curves, which change with the variations of corresponding parameters, and the interpretation and selection based on these features of intensity curves are specified as follows:

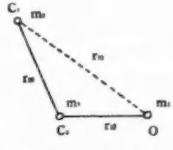
TABLE III B

THE MOLECULAR MODELS AND CORRESPONDING ASSUMED MOLECULAR CONSTANTS FOR ISOPROPYL CHLORIDE

Models	C—C (Å)	C—Cl (Å)	∠CCC°	∠CCCl°	$q/q_{0.5s}$
A	1.54	1.75	109.5	109.5	1.006_0
B	〃	〃	112	109.5	1.006_8
C	〃	〃	112	112	0.989_0
D	〃	〃	114	112	(0.994_7)
E	1.54	1.77	112	108	(1.011_7)
F	〃	〃	109.5	109.5	1.002_5
G	〃	〃	114	112	0.984_7
P	1.52	1.77	109.5	109.5	(1.016_3)
Q	1.56	1.77	〃	〃	0.993_9
H	1.54	1.80	109.5	109.5	0.990_9

1) For the groups of curves from A to D and E to G, the angles ∠CCC and ∠CCCl increase in an orderly way in each group from A to D and E to G. The C-Cl distances are 1.75 Å and 1.77 Å respectively, and other parameters, C-C and rotational configuratione, remain constant.

When compared with those of the visual curve, nearly equal heights of the seventh



5) P. C. Cross and J. H. Van Vleck [*J. Chem. Phys.* **1**, 350 (1933)] have calculated that the parameters of the equation, $V=1/2\,c_{12}(\Delta r_{12})^2+c_{23}(\Delta r_{23})^2+c_{13}(\Delta r_{13})^2$, are $c_{12}=4.0\times10^5$dyne/cm., $c_{13}=3.5\times10^5$, and $c_{12}=1.7\times10^5$dyne cm, respectively, where V is the potential function for the ethyl alcohol molecule (XXY type molecule), Δr_{ij}'s denote the displacements of interatomic distances as shown in the figure.

6) V. Schomaker et al., *J. Am. Chem. Soc.*, **73**, 1482 (1951).

7) M. Kimura, *J. Chem. Soc. Japan.* **71**, 18 (1950) (Japan).

8) O. Bastiansen, *Acta Chem. Scand.*, **3**, 415 (1949).

9) M. Kimura and M. Yamaha, the work was reported in the First Annual Meeting of the Chemical Society of Japan, April 3rd, 1948 (at Tokyo University, Tokyo).

10) J. Ainsworth and J. Karle, *J. Chem. Phys.*, **20**, 425 (1952).

TABLE IV B

OBSERVED q-VALUES AND CALCULATED $q/q_{obs.}$ VALUES FOR BETTER MOLECULAR MODELS OF ISOPROPYL CHLORIDE

Max.	Min.	q_{obs}	wt.	A	B	C	F	Q
	2	(13.66)		(0.908)	(0.922)			(0.930)
2		16.55	1	1.003	1.009	0.982	1.015	0.997
	3	20.72	1	0.982	0.980	0.965	1.014	0.965
3		23.97	2	1.008	1.010	0.989	1.030	0.997
	4	28.10	1	0.982	0.980	0.959	1.012	0.966
4		30.82	2	0.980	0.980	0.964	1.003	0.972
	5	35.12	1	0.978	0.974	0.968	0.978	0.974
5		38.63	3	1.015	1.015	1.003	1.004	1.002
	6	42.59	2	1.021	1.017	0.997	0.997	1.006
6		46.25	3	1.012	1.012	0.995	0.995	1.002
	7	50.54	2	1.005	1.003	0.989	0.995	0.999
7		54.55	2	1.001	1.007	0.982	0.999	0.999
8		59.56	2	1.017	1.021	1.002	1.004	1.006
	9	63.60	2	1.022	1.022	1.008	1.009	1.011
9		68.60	3	1.010	1.013	0.997	1.001	0.997
	10	72.83	1	1.011	1.013	0.989	1.002	0.998
10		(77.31)	1	0.995	0.999	0.962	0.979	0.986
11		82.24	1	(1.010)	(1.010)	0.998	1.001	1.013
12		(92.33)		(1.007)	(1.007)	(1.045)	(1.001)	(0.996)
	Weighted mean:			1.006_0	1.006_8	0.989_0	1.002_5	0.990_9
	Wtd. mean sq. deviation:			0.012_9	0.013_5	0.014_4	0.010_9	0.013_9

and the eighth maxima, the small shelf-like tenth maximum on the eleventh maximum and the position of the twelveth maximum, the features in the curves A, B, E and F seem to be satisfactory. For angles ∠CCC and ∠CCCl≧112°, the features above pointed out become less satisfactory while further deviations occur, as shown in the curves D and G.

2) Curves P and Q, having constant C-Cl =1.77Å and ∠CCC=∠CCCl=109.5°, show the changes of *q-values* according to the variation of C-C distances, from 1.52Å to 1.56Å. The $q/q_{obs.}$ values of curve Q are almost acceptable, but the values of P are so large that it seems to be out of the range of errors.

3) On the curves A, F and Q, the contributions of the rotational configurations of methyl groups appear in the range $10<q<35$. The broken curve on each curve corresponds to the eclipse form of each model, and real curves in the same q-range correspond to the staggered form. By the visual method, it is hardly possible to determine exactly the intensity ratio of the second to the third maxima, because of the coexistence of background in the q-range. So the difference of this ratio which appears in the theoretical intensity curves is not remarkable enough for us to distinguish it.

4) The effects of vibration factors are approximately taken into account in all the cases A to H. Dotted curves on A, B and C in the range $40<q$ show the curves in which these factors are neglected, i.e. they correspond to the rigid models. The damping effect agrees roughly with the visual curve in the intensity relations of maxima and minima in the range $q>60$, that is, the pictures from the curves including the factors seem to require the tenth maximum to be lower and the tenth and the eleventh minima to be shallower than the respective lines joining the mentioned adjacent features of the curves in which the factors are ignored.

Various molecular parameters obtained from this investigation seem nearly to agree with and confirm those from the previous data[1], in which the results were obtained from the observation of maxima and minima up to the range $q<50$, because the observation of this report has been obtained from wider range up to $q<95$, in which the variations of features of intensity relations are conspicuously clear in this range ($50<q<95$).

Results and Discussions

From these considerations above pointed out, the models corresponding to the curves B_S, P_S, Q_S, Y_S and Y_E for isopropyl alcohol and C, D, G, P and R for isopropyl chloride are at least to be rejected in our experiment.

We have obtained the final results as follows:

Isopropyl alcohol, C−O : 1.45±0.03Å, C−C : 1.54±0.02Å, ∠CCC≈∠CCO : 110±2.5° and

the angle ∠CCO and ∠CCC are not equal to or larger than 112° simultaneously. And also the relative equilibrium position of the methyl groups against the central –CHOH group is not at least the rigorously staggered position.

Isopropyl chloride, C–Cl : 1.76±0.02Å, C–C : 1.55±0.02Å and ∠CCC≈∠CCCl : 109.5 ±1.5°.

These conclusions are reasonable, except in the case of the equilibrium position of methyl groups in the isopropyl alcohol molecule, compared with the structures of several related compounds of these molecules, but some discrepancies are found, for example, in comparison with the results of 1, 2-dichloropropane molecule by V. Schomaker et al.[14] which have shown the values 1.56Å and 1.79Å for C-C and C-Cl distances respectively.

From the results of this investigation, it seems to be hoped that we could obtain some aspects about the problems of methyl groups from the electron diffraction investigations, if we would choose adequate samples and could determine the intensity relations more quantitatively.

Summary

The molecular structures of isopropyl alcohol and chloride have been investigated by the electron diffraction method. The atomic distances, C-O : 1.45±0.03Å, C-C : 1.54±0.02Å and valence angles, ∠CCC≈∠CCO : 110°±2.5° are determined for the former molecule, and distances C-Cl : 1.76±0.02Å, C-C : 1.55±0.02Å and angles ∠CCC≈∠CCCl : 109.5±1.5° for the latter.

The approximate thermal vibration factors have been taken into account for the determination of the best molecular models. The rotational configurations of methyl groups have been considered, but the equilibrium position of two methyl groups cannot be determined conclusively, in spite of the fact that this effect upon the intensity curves are not to be ignored in the case of isopropyl alcohol molecule.

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Chemical Institute, Faculty of Science,
Tokyo University of Education,
Ootsuka, Tokyo, Japan

11) J. W. Coutts and L. Livingston, *J. Am. Chem. Soc.*, **75**, 1542 (1953).
12) M. Yamaha, this work was reported in the sixth Annual Meeting of the Chem. Society of Japan, April 4th, 1953 (at Kyoto Univ.).
13) W. Gordy et al., *J. Chem. Phys.*, **20**, 605 (1952), (Microwave spectroscopy).
14) V. Schomaker et al., *J. Chem. Soc.*, **20**, 555 (1952).
15) W. F. Edgell et al., *J. Chem. Soc.*, **16**, 1002 (1948), (Microwave spectroscopy), cf. W. Shard and R. A. Spur, *J. Am. Chem. Soc.*, **66**, 16 (1944).
16) See. J. R. Nielsen and C. M. Richards, *J. Chem. Phys.* **16**, 67 (1948).

The Dipole Moments of Some Polyhalocyclohexanes and their Related Compounds. I.

By Ichiro MIYAGAWA, Yonezo MORINO, and Randolph RIEMSCHNEIDER

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As is well known, it is possible for the atoms attached to a carbon atom of the cyclohexane ring to exist at two positions: the polar and the equatorial ones, with regard to the relative direction of the bonds to the plane of the ring.[1,2,3a)] It follows that a poly-substituted compound of cyclohexane has a lot of geometrical isomers. A good example is the case of BHC: it has actually six isomers, α to η forms,[4)] due to the various combinations of the polar and equatorial bonds, and its γ-isomer is characterized by its mar-

1) O. Hassel and E. Naeshagen, *Tids. Kjemi Bergvesen Met.* **10**, 126 (1930).
2) K. Kojima and T. Yoshino, *J. Am. Chem. Soc.*, **75**, 166 (1953).
3) R. Riemschneider, a) Communication XXI. . . . The method of representation of the chair form of cyclohexane ring described in Comm. XXI is not used in the present paper; b) Comm. X, *Monat Chem.*, **83**, 394 (1952) and Comm. XXII, *Zeit. Naturforschung*, **8b**, 000 (1953); c) Comm. XXIII, ibid. **8b**, 000 (1953); d) Comm. XXV, ibid., **8b**, 161 (1953); e) Comm. XXVII, *Monat. Chem.*, **84**, 512 (1953); f) Comm., III and IV, *Zeit. Naturforschung*, **5b**, 307 (1950) and **6b**, 48 (1951).
4) As for η-BHC of the configuration of e.e.p.e.p.p. compare: R. Riemschneider, Komm., XXIV, *Monat. Chem.* **84**, 000 (1953).

vellous power as an insecticide.

Thus the determination of the geometrical configuration of the isomers of these compounds is most desirable, but it usually requires much time. As the halogen-carbon bond has a large dipole moment, its measurement would afford an effective means for this purpose, as in the case of the isomers of BHC.[5]

The critical discussions of the structure of the compounds stated here have already been presented elsewhere by one of the present authors (R.R.)[3b-f], also taking into account the dipole moment. The aim of this paper is to report the details of the measurement as well as the full information of the calculation.

Experimental

Materials All the samples measured had been prepared by one of the present authors (R.R.)[3b-f] and their dipole moments were measured by another (I. M.) without further purification.

The solvent benzene was made free from thiophene by aluminium chloride, dried over metallic sodium and then distilled, the fraction boiled within 0.1°C being collected for use.

Measurement The density d and dielectric constant ε of the solution in benzene were measured with a pycnometer and a heterodyne beat apparatus in a manner previously described.[5] The wavelength used was about 150 meters. The polarization $p_{2\infty}$ of the solute was calculated by the following formula derived by Halverstadt-Kumler's method[6]:

$$p_{2\infty}=\frac{\varepsilon_1-1}{\varepsilon_1+2}\frac{1}{d_1}\left[1+\frac{3a}{(\varepsilon_1-1)(\varepsilon_1+2)}-\frac{b}{d_1}\right] \quad (1)$$

where ε_1, and d_1 are respectively the dielectric constant and density of the solvent, and a and b are the coefficients of the linear expansion of dielectric constant and density of the solution with respect to the weight fraction w:

$$\varepsilon=\varepsilon_1+aw, \quad (2)$$

and

$$d=d_1+bw. \quad (3)$$

Then the dipole moment μ is given by the equation:

$$\mu=0.0128\left[(P_{2\infty}-P_E-P_A)\,T\right]^{1/2}, \quad (4)$$

where $P_{2\infty}=M_2p_{2\infty}$ is the molecular polarization, (M_2 being the molecular weight), P_E and P_A are the electronic and atomic polarization of the solute respectively. P_E was taken to be equal to the molar refraction MR_D for sodium D line, which was calculated by the use of the atomic refraction given in "Landolt-Börnstein Tabellen" and P_A was assumed to be 5 percent of MR_D.

The temperature of the thermostat was kept all through at 30°C, because at the time when this measurement was undertaken the room temperature sometimes exceeded 25°C.

5) Y. Morino, I. Miyagawa, and T. Oiwa, *Botyu-kagaku*, **15**, 181 (1950).

6) I. F. Halverstadt and W. D. Kumler, *J. Am. Chem. Soc.*, **64**, 2988 (1942).

Results

The weight fraction of the solute, w, the dielectric constant, ε and the density, d, of the solution are given in Table I, together with the coefficients a and b calculated from them. The molecular polarization, $P_{2\infty}$, and the dipole moment μ thus obtained are listed in Table II.

TABLE I

DIELECTRIC CONSTANTS AND DENSITIES OF BENZENE SOLUTIONS AT 30°C

w	ε	d
1. Tetrabromodichlorocyclohexane, $C_6H_8Cl_2Br_4$, m. p. 203°.		
0.00000	2.2615	0.8685
0.01814	2.2823	0.8789
0.02971	2.2947	0.8865
	$a=1.11_9$	$b=0.603$
2. Dibromotetrachlorocyclohexane, $C_6H_8Cl_4Br_2$, m. p. 178°.		
0.00105	2.2738	0.8742
0.01937	2.2846	0.8792
0.03143	2.3007	0.8862
0.04298	2.3142	0.8923
	$a=1.22_3$	$b=0.555$
3. Dibromotetrachlorocyclohexane, $C_6H_8Cl_4Br_2$, m. p. 285°.		
0.01092	2.2632	0.8738
0.01894	2.2644	0.8777
	$a=0.153$	$b=0.487$
4. Decachlorocyclohexene, C_6Cl_{10}, m. p. 95°.		
0.01464	2.2646	0.8755
0.02455	2.2668	0.8809
0.03551	2.2692	0.8865
0.05274	2.2728	0.8955
	$a=0.214$	$b=0.511$
5. Octachlorocyclohexane, $C_6H_4Cl_8$, m. p. 93°.		
0.01328	2.2755	0.8742
0.02259	2.2858	0.8791
0.04094	2.3053	0.8879
0.06166	2.3274	0.8983
	$a=1.069$	$b=0.475$
6. $C_3H_5O_2Cl$, m. p. 123-124°		
0.01371	2.3661	0.8724
0.02393	2.4425	0.8762
0.03737	2.5404	0.8809
0.05014	2.6324	0.8856
	$a=7.39_7$	$b=0.359$
7. 2, 2, 6, 6,-Tetrachlorocyclohexanone, $C_6H_6OCl_4$, m. p. 84°.		
0.01371	2.3757	0.8737
0.02772	2.4980	0.8789
0.04252	2.6300	0.8846
0.05905	2.7803	0.8910
	$a=8.98_1$	$b=0.381$

8. 1,4-Dichlorocyclohexadiene-(1,4), $C_6H_6Cl_2$, m. p. 63°.

0.03516	2.2661	0.8778
0.05975	2.2694	0.8844
	$a=0.132$	$b=0.265$

TABLE II

MOLECULAR, ELECTRONIC, AND ATOMIC POLARISATIONS, AND DIPOLE MOMENTS AT 30°C

Compounds	m.p.	$P_{2\infty}$(cc)	P_E+P_A (cc)	μ(D)
Tetrabromodichlorocyclohexane	203	148.0	71.9	1.93
Dibromotetrachlorocyclohexane	178	135.4	65.8	1.84
Dibromotetrachlorocyclohexane	285	67.8	65.8	0.3
Decachlorocyclohexene	95	77.2	75.9-79.9	0.
Octachlorocyclohexane	93	128.8	70.0	1.69
$C_6H_5O_2Cl$	123-124	236	34.2	3.14
2,2,6,6-Tetrachlorocyclohexanone	84	451	50.0	4.40
1,4-Dichlorocyclohexadiene-(1,4)	63	39.1	37.2	0.3

1. **Tetrabromodichlorocyclohexane $C_6H_7Cl_2Br_4$ m. p. 203° and Dibromotetrachlorocyclohexanes, $C_6H_8Cl_4Br_2$ m. p. 178° and 285°.** Judging from the method of preparation of these compounds, there is no doubt that they are 1, 2, 3, 4, 5, 6-substituted ones,[3b-e] exactly similar to BHC, though the accurate positions of the bromine atoms are not definitely assigned. The spacial configurations of the six isomers of BHC are schematically shown in Fig. 1, where the cyclohexane ring is represented by a hexagonal ring, the chlorine atom in an equatorial bond (e-bond) by a short line, the chlorine atom in a polar bond (p-bond) by a small circle on the hexagonal ring, the white and black circles denoting chlorine atoms above and below the central plane.

Now the moments of these compounds are considered to be nearly the same as, or slightly smaller than, those of the corresponding isomers of BHC, since the bond moment of the C–Br bond is nearly the same as that of the C–Cl bond. The moments of the isomers of BHC were found to be α: 2.2 D, β: 0 D, γ: 2.8 D, δ: 2.2 D, and ε: 0 D. The moment of η-isomer has not been measured, but according to the rule suggested by Y. Morino, I. Miyagawa, and T. Oiwa,[5] it is estimated to be 1.88 D. Therefore, the observed values of the dipole moments of $C_6H_6Cl_2Br_4$, m.p. 203° (1.93 D) and of $C_6H_6Cl_4Br_2$, m.p. 178° (1.84 D) apparently indicate that they are neither β nor ε, but α, δ or η type compounds. The η-form may be safely eliminated from our consideration, because the abundance of the corresponding chlorine compound is extremely small. It can not be discriminated, however, whether they are of α-type or of δ-one.

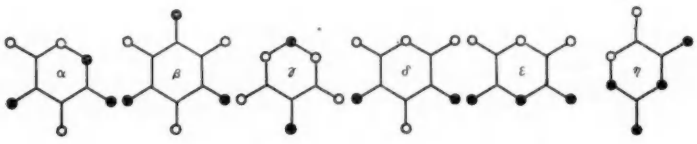
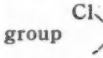
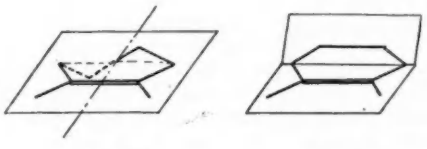


Fig. 1. Configuration of the Isomers of BHC.

Similarly it is concluded that $C_6H_8Cl_4Br_2$, m.p. 285° is of β type or of ε one, since its moment is negligibly small. Considering the fact that its melting point is as high as that of the β-isomer of BHC (310°), it seems probable that $C_6H_8Cl_4Br_2$, m.p. 285° has the configuration of β-form.

2. **Decachlorocyclohexene, C_6Cl_{10}.** For the cyclohexene ring two forms should be considered: first, the C_2 form corresponding to the chair form of the cyclohexane ring, and second, the C_s form corresponding to the boat form (See Fig. 2). The dipole moments for both forms are calculated to see which form is actually realized in this case. The assumptions used are as follows: the moment of the group  is 1.74 D, located in the plane ClC=CCl and perpendicular to the double bond. The moments of the C–Cl bonds attached to other carbon atoms are 1.86 D. At the same time the induction effect suggested by us[5] are taken into account it is assumed that the C–Cl bond which is marked



C_2-form C_s-form

Fig. 2. The two forms Cychohexene Ring

by a circle in Fig. 3, induces at each bond in the direction along the bond the moment shown in the figure, the moments induced perpendicularly to the bonds being all disregarded. Of course this rule is an empirical one, but it has served to enable us to compute with reasonable accuracy not only the moments of fourteen chlorinated aliphatic hydrocarbons but also those of eleven compounds which have a cyclohexane ring.

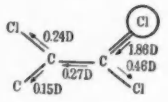


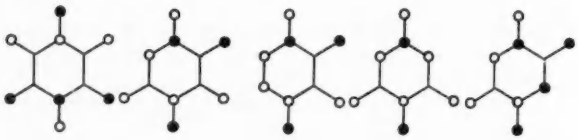
Fig. 3. The Induction Moments due to C–Cl Dipole

The calculated values of the dipole moments by use of these assumptions are found to be 0.40 D for C_s form and 0.14 D for C_2 form. Both of them lie in the allowed region from the observed value 0D, so that the configuration of the cyclohexene ring can not be decided by this discussion.

Though the present calculation gave no discrimination between the two forms, it has the merit of providing a strong evidence that in the vector addition for computing the dipole moment of a molecule, the induction effect can by no means be put out of the consideration, because, otherwise, it will result in values larger even than 2D for decachlorocyclohexene, in sharp contrast to the observed zero moment.

3. **Octachlorocyclohexane, $C_6H_4Cl_8$, m.p. 93°.** The sample was prepared by the chlorination of *p*-dichlorobenzene.[3e] It is evident that it is 1,1,2,3,4,4,5,6-substituted compound, so that the geometrical configuration of this compound must be one of the following five forms:

(1)	(1pe, 2e, 3e, 4pe, 5e, 6e)	0 D
(2)	(1pe, 2p, 3e, 4pe, 5e, 6e)	1.47 D
(3)	(1pe, 2p, 3p, 4pe, 5e, 6e)	1.86 D
(4)	(1pe, 2p, 3e, 4pe, 5e, 6p)	1.93 D
(5)	(1pe, 2p, 3e, 4pe, 5p, 6e)	0 D



(1) (2) (3) (4) (5)

Fig. 4. The Configurations of the Isomers of Octachlorocyclohexane

Their spacial configurations are illustrated in Fig. 4. The computed moments of these isomers are also given in the above, the assumptions for the calculation being the same as those used in the preceding case. The observed value, 1.69 D, suggests that it is neither (1) nor (5), but one of (2), (3), and (4). It cannot be confirmed which one of them should be assigned to $C_6H_4Cl_8$, m.p. 93°, but the most stable form (2) may be the most favourable. The reason is that the form (2) has one pair of polar C–Cl bonds, while the form (3) has two pairs and the form (4) three pairs of them. The most important part of the intramolecular potential energy of this molecule may be due to the steric repulsion between this pair of polar C–Cl bonds, which project toward the same direction at a very close proximity. The difference 0.22 D between the calculated and the observed may be ascribed to the rough approximation of the calculation.

4. **Tetrachlorocyclohexanone, $C_6H_6OCl_4$.** It was prepared by the chlorination of cyclohexanol, and the substitution by chlorine atoms was confirmed to take place at 2,2,6,6-positions.[3d] In order to estimate the dipole moment of this molecule, some additional assumptions are necessary for the value of C=O moment itself and the induction effect due to C=O bond, besides the induced moments by C–Cl bond shown in Fig. 3. The C=O bond moment may be taken to be 2.80 D from the moment of cyclohexanone.[8] If we tentatively assume for the induction effect upon and by the C=O bond the same amounts as those of the C–Cl bond, then 3.78 D is obtained for the total moment of this molecule.* The discrepancy between this and the observed value, 4.40 D, should, of course, be attributed to the provisional assumptions for the induced moment. In fact, larger induced moments should be assigned to them, since the bond moment of C=O is larger than that of the C–Cl bond. If the moments induced by the C=O dipole are increased by the ratio 2.80 / 1.86,** (Fig. 5 shows the individual values of the induced moments in this case), the computed values of the moment of this molecule becomes 4.21 D.

8) J. W. Williams *J. Am. Chem. Soc.* **52** 1831 (1930).

* The valency angles are all assumed to be tetrahedral.

** The moment induced at the C=O bond C-Cl bond remains 0.24 D, the same as that at the C-Cl bond.

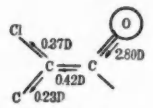
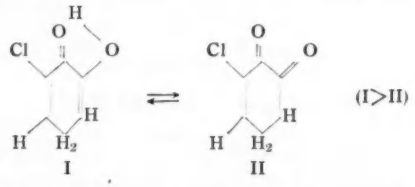


Fig. 5. The Induction Moments due to C=O Dipole

5. $C_5H_5O_2Cl$, m.p. 123-124° from 2,2,6,6-Tetrachlorocyclohexanone.[4d] It has been found that this compound has the following two tautomers in equilibrium in the ratio of I>II.[3d]



(I>II)

In order to make sure of this conclusion, the moments of the two forms (I) and (II) are calculated by the ordinary assumptions that C–Cl : 1.60 D, C–O : 1.10 D, C=O : 2.80 D, O–H: 1.53D, ∠HOC : 100°, and the bonds C–Cl, C=O, and O–H are all located in one plane,* and that the induced moments are the same as those of 2,2,6,6-tetrachlorocyclohexanone, which gave 3.78 D for its moment. The calculated moment of the form I is 1.98 D, and that of the form II is 4.33 D.** Thus, in order to explain the observed moment 3.14 D, it must be assumed that the forms I and II coexist in equilibrium at the ratio of 60 % to 40 %. Needless to say, no great credit should be laid to the value of this ratio,*** since the moments of the two forms used for the calculation are based upon many hypothetical assumptions. Yet it is enough to support the conclusion stated above that this compound is a tautomeric mixiure of the two forms, form I predominating.

6. 1,4-Dichlorocyclohexadiene-(1,4).[3j] Since the four bonds attached to the ethylenic carbon atoms are located in one plane, this molecule has to be folded by the axis through the central two carbon atoms. If the angle ∠C=C–Cl be denoted by θ, and the angle between the two planes by φ (See Fig. 6), then the resultant moment is simply given by

$$\mu = 2\mu_{cct} \sin\theta \sin\frac{1}{2}(\pi - \varphi)$$

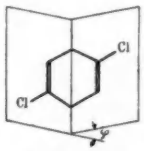


Fig. 6. The Configuration of 1,4-Dichlorocyclohexadiene-(1,4)

Therefore, inserting the value of μ=0.30 D, together with μ_{cct}=1.60 D, and θ=120°, we get φ=14°.

On the other hand, if we assume the angle of ∠C=C–C to be 120°, and the angle of ∠C–C–C of the central carbon atoms to be tetrahedral, then the angle between the two planes is geometrically obtained to be 40°. At a glance, it seems that there exists a serious difference between the calculated and the observed, but, if some allowance be made for the valency angles, the observed value of φ stated above can be brought into the allowed region of the molecular model. For instance, the application of the the angles ∠C=C–C : 123°, and ∠C–C–C : 112°, gives φ=17° instead of 40°. In fact, the widening of the valency angle are readily acceptable if we consider the fact that the repulsion between the nonbonded carbon atoms has the possibility of making the valency angles wider by a few degrees.

Here it should be noted that the values of φ computed from the dipole moment may have some errors, because the observed moment is so small that the values obtained for the angle are greatly affected by the assumption employed for the atomic polarisation. If we take $P_E+P_A=MR_D$ in place of 1.05 MR_D, the moment will increase to 0.42 D, resulting in the increase of the angle to 20°. Thus it can be concluded that the cyclohexadiene-(1,4) ring is folded, but flatter than expected by an ordinary tetrahedral angle.

Department of Chemistry,
Faculty of Science,
Tokyo University,
and Chemisches Institut der
Freien Universität, Berlin-Dahlem

* It can be easily shown that the actual deviation from the plane is virtually small.

** The interaction of two double bonds in the conjugated position is not considered for the time being.

*** The complete neglect of the induction effect provides 2.65 D and 5.11 D for the moment of the two forms, resulting in 85% to their concentrations.

The Studies of Molecular Structures by Electron Diffraction. III. The Structures of m- and p Difluorobenzene

By Hajime OOSAKA†, Hiroshi SEKINE and Takahide SAITO

(Received January 26, 1954)

Introduction

The results of the recent electron diffraction studies on the carbon-fluorine distances in aromatic compounds are collected in Table I.

TABLE I

THE PREVIOUS RESULTS OF THE C–F DISTANCES OF FLUORINE-CONTAINING AROMATIC COMPOUNDS

Substance	C–F distance (Å)	Reference
C_6H_5F	1.34 ± 0.04	1
C_6H_5F	1.31 ± 0.03	2, 4
o-$C_6H_4F_2$	1.35 ± 0.03	1
p-$C_6H_4F_2$	1.31 ± 0.03	3
o-C_6H_4FCl	1.31 ± 0.03	3
p-C_6H_4FBr	1.30 ± 0.03	3

As shown in it, one of us[1] reported that the distance is shorter in monofluorobenzene and *o*-difluorobenzene than in aliphatic compounds, but soon later Hassel[2] reported an even shorter distance in monofluorobenzene, which seemed compatible with the recent data of chlorine-or bromine-containing compounds[3]. In these, it is difficult to determine the precise C—F distance, because the chlorine or bromine atom has much greater scattering power than fluorine. That is the reason why we feel an interest in the difluorosubstitutes, although we may find different C—F distances from the monofluorobenzene.

Experimental

The samples, *m*-difluorobenzene[5] and *p*-difluorobenzene,[6] were prepared by the Schiemann reaction. They showed the boiling points 82°C. and 88°C., respectively.

The camera length is about 9.1 cm. The electron wave length, about 0.055 Å, was calibrated with gold foil diffraction.

Interpretation

The diffraction photographs were interpreted by the usual visual method. For the calculation of the theoretical intensity curves, the formulae

$$I(q) = k \sum_i \sum_j \frac{Z_i Z_j}{r_{ij}} \exp(-a_{ij} q^2) \sin \frac{\pi}{10} q r_{ij}$$

$$q = (40/\lambda) \sin(\theta/2) \qquad a_{ij} = (\pi^2/200) l_{ij}^2$$

are used, where r_{ij} is the distance between the i-th and j-th atom, λ is the electron wave length, θ is the scattering angle, Z_i is the atomic number of i-th atom, and l_{ij} is the mean amplitude of r_{ij}. The thermal vibration terms are neglected as a first approximation, i.e., we put $l_{ij}=0$. It is assumed that the hydrogen and fluorine atoms are coplanar with the regular hexagon benzene ring, and that the distances of C—C and C—H are 1.39 Å. and 1.08 Å. respectively. All the interference terms except those of hydrogen atoms are taken into account. The five theoretical curves calculated for these molecules with C—F distances of 1.27, 1.29, 1.31, and 1.35 Å and a visual intensity curve obtained by photographs are compared in Fig. 1 and 2. The values of q of the observed and calculated maxima, and their ratios $q_{calc.}/q_{obs.}$ are given in Table II and III.

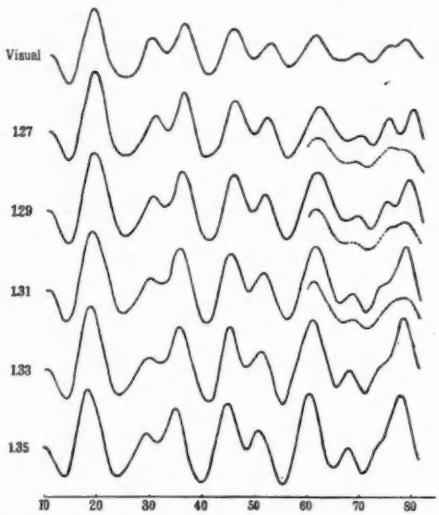


Fig. 1. The visual and theoretical curves of *m*-Difluorobenzene.

1) H. Oosaka, This Bulletin, **15**, 31 (1940).
2) O. Hassel and H. Viervoll, *Acta chemica Scand.*, **1**, 149 (1947).
3) H. Oosaka and Y. Akimoto, This Bulletin, **26**, 433 (1953).
4) T. Yuzawa and M. Yamaha, This Bulletin, **26**, 414 (1953).
5) G. Schiemann and T. Pillarsky; *Ber.* **62**, 3039 (1929), 3035 (1929).
6) P. Ruggli and E. Capser, *Helv. Chim. Acta.* **18**, 1414 (1435).
7) I. Karle, *J. Chem. Phys.*, **20**, 65 (1952).
8) Y. Morino and Kuchizu, private communication.

TABLE II

$q_{calc.}/q_{obs.}$ OF *m*-DIFLUOROBENZENE

	C–F	1.27	1.29		1.31		1.33
Max.	$q_{obs.}$	$q_{calc.}/q_{obs.}$	$q_{calc.}/q_{obs.}$		$q_{calc.}/q_{obs.}$		$q_{calc.}/q_{obs.}$
1	18.5	1.011	1.005		1.000		0.995
2	29.6	1.024	1.020		1.017		1.014
3	35.9	0.994	0.989		0.983		0.981
4	45.2	1.011	1.007		1.002		0.998
5	52.1	0.996	0.992		0.989		0.984
6	61.0	1.012	1.008	1.005+	1.003	1.000+	1.000
7	68.8	1.016	1.006	0.999	0.999	0.991	0.994
8	74.8	1.004	1.000	1.006	0.996	1.006	0.992
9	78.5	1.013	1.006	0.996	1.000	0.993	0.996
Arithmetical mean		1.009	1.003	1.002	0.999	0.998	0.995
Mean square root deviation		±0.009	±0.009	±0.009	±0.007	±0.007	±0.009

+: These values were estimated from the dotted curves in Fig. 1, which contained the thermal vibrational terms.

Finally, as a second approximation, the thermal vibration terms l_{ij}, roughly estimated (in Table IV) in reference to the calculated aliphatic data,[7,8] are introduced into the most probable three models, for $q \geq 60$. (The values $q_{calc.}/q_{obs.}$ are given in Table II and III.)

The radial distribution function is not calculated, since the C—F distance is the only one variable.

Details and Results

(a) ***m*-Difluorobenzene** (Fig. 1 and Table II). In glancing over the intensity curves, the models for C—F=1.29, 1.31 and 1.35 Å seem right. According to the careful examination of these models on the relative intensities of the corresponding maxima, especially max. VII, the $q_{calc.}/q_{obs.}$ values, and their mean deviations, it is reasonable for the C—F distances of *m*-difluorobenzene to be 1.30±0.03 Å.

(b) ***p*-Difluorobenzene** (Fig. 2 and Table III). A procedure similar to the above, leads us to the conclusion that the C—F distance of this molecule is 1.30±0.03 Å.

They agree well with the results of the previous investigations.

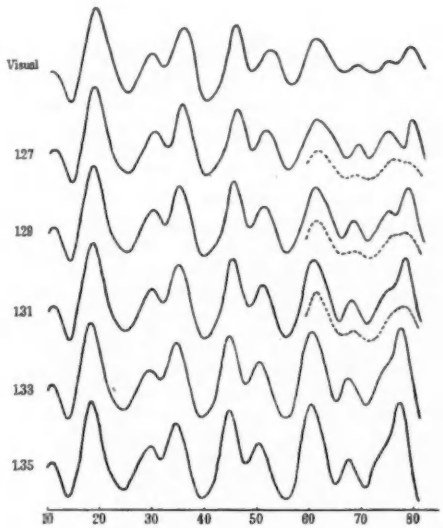


Fig. 2. The visual and theoretical curves of *p*-Difluorobenzene.

TABLE III

$q_{calc.}/q_{obs.}$ OF *p*-DIFLUOROBENZENE

	C–F	1.27	1.29		1.31		1.33
Max.	$q_{obs.}$	$q_{calc.}/q_{obs.}$	$q_{calc.}/q_{obs.}$		$q_{calc.}/q_{obs.}$		$q_{calc.}/q_{obs.}$
1	18.5	1.016	1.011		1.005		1.005
2	29.5	1.027	1.024		1.017		1.014
3	35.8	0.992	0.986		0.980		0.975
4	45.6	1.007	1.002		0.996		0.991
5	52.3	0.987	0.985		0.979		0.973
6	61.1	1.002	1.000	1.000+	0.998	1.000+	0.997
7	68.9	1.004	0.993	0.991	0.988	0.984	0.985
8	74.8	1.005	1.007	1.009	1.005	1.004	0.999
9	79.0	1.008	1.000	1.000	0.995	0.995	0.989
Arithmetical mean		1.005	1.001	1.001	0.996	0.996	0.991
Mean square root deviation		±0.011	±0.012	±0.012	±0.012	±0.011	±0.012

+: These values were estimated from the dotted curves in Fig. 2, which contained the thermal vibrational terms.

TABLE IV
THE COEFFICIENTS OF THE THERMAL VIBRATIONAL TERMS; a_{ij}

$a_{ij} = 0.04935 \times l_{ij}^2$

Atomic pair	a_{ij}	Atomic pair	a_{ij}
C—C	0.000049	C—F	0.000089
C···C′	0.000064	C···F′	0.000160
C···C″	0.000089	C···F″	0.000253
C—H	0.000128	C···F‴	0.000287
C···H′	0.000226	H—F	0.000130
C···H″	0.000400	$(H\cdots F)_m$	0.000240
C···H‴	0.000460	$(H\cdots F)_p$	0.000350
		$(F\cdots F)_m$	0.000260
		$(F\cdots F)_p$	0.000350

Summary

The C—F distances of *m*-difluorobenzene and *p*-difluorobenzene are investigated to be almost equal, 1.30±0.03 Å.

We have great pleasure in acknowledging our debt of gratitude to Professor A. Kotera for his continued encouragement during this research. We wish to express our thanks to Mr. M. Yamaha, Mr. M. Igarashi and Mr. Y. Akimoto for their helpful discussions and suggestions.

Chemical Laboratory, Tokyo Bunrika University, Tokyo

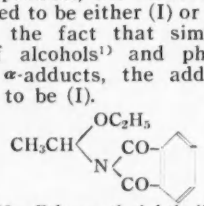
LETTER

Addition Reactions of Amino Compounds to Ethyl Vinyl Ether

By Junji FURUKAWA, Akira ONISHI, Teiji TSURUTA, and Shiro OSHIMA

(Received November 27, 1953)

A new product (A) was obtained in the reaction between phthalimide and ethyl vinyl ether without any added catalyst. The analysis and the molecular weight determination suggest that (A) is likely to be an addition product, the structure of which being assumed to be either (I) or its β-isomer. In view of the fact that similar addition reactions of alcohols[1] and phenols[2] form acetals, the α-adducts, the adduct (A) may be expected to be (I).



(I) N-α-Ethoxyethylphthalimide

On decomposition by hydrochloric acid, the adduct (A) gave rise to acetaldehyde along with phthalimide. The formation of acetaldehyde is in favor of the structure of N-α-isomer (I).

A similar addition product (B) has likewise been obtained from a reaction with carbazole as the amino component. On the other hand, Voronkov[3] reported that vinyl ethers condense with monocarboxylic acid amides to yield ethylidene-di-O-acylamide, $CH_3CH[OC(=NH)R]_2$, in the presence of hydrochloric acid. The structure of the O-acylamide type is obviously excluded from the possible structures for the adduct (B), but is not for the adduct (A).

It was found that vinyl acetate also may condense with phthalimide to give rise to a similar adduct.

Detailed examinations as to the structure of the adducts as well as experiments on the reactions between vinyl compounds and various amino compounds (imides, amides and amines) are now in progress in our laboratory.

Experimental

A mixture of 22.0 g. (0.15 mol.) of phthalimide and 32.4 g. (0.45 mol.) of ethyl vinyl ether was heated at 155° for 5 hours in a 100 cc.-autoclave. Evaporating the unreacted vinyl ether, a viscous oily residue was obtained, which gradually turned into a crystalline matter. The yield of the adduct was quantitative. Being recrystallized from petroleum benzine and alcohol, colorless crystals (A) were obtained which showed m.p. 64~65°. *Anal.* Calcd. for (I), $C_{12}H_{13}O_3N$: C, 65.74, H, 5.98, N, 6.39. Found: C, 65.92, H, 5.52, N, 6.82. *Molecular weight*: Calcd. 219.23; Found: 216 (cryoscopic method). Boiling 5 g. of (A) with 14 cc. of hydrochloric acid (1:1), phthalimide and acetaldehyde were formed in almost equimolecular amount, which were identified by mixed melting with authentic specimens of the imide and of the 2.4-dinitrophenylhydrazone, respectively.

The experiment for carbazole was essentially the same as stated above.

This work was supported by a grant in aid for the Miscellaneous Scientific Research from the Ministry of Education.

Institute for Chemical Research, Kyoto University, Takatsuki, Osaka

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